ELEMENTS

OF

CHEMISTRY

SHEPARD

BRIEFER COURSE

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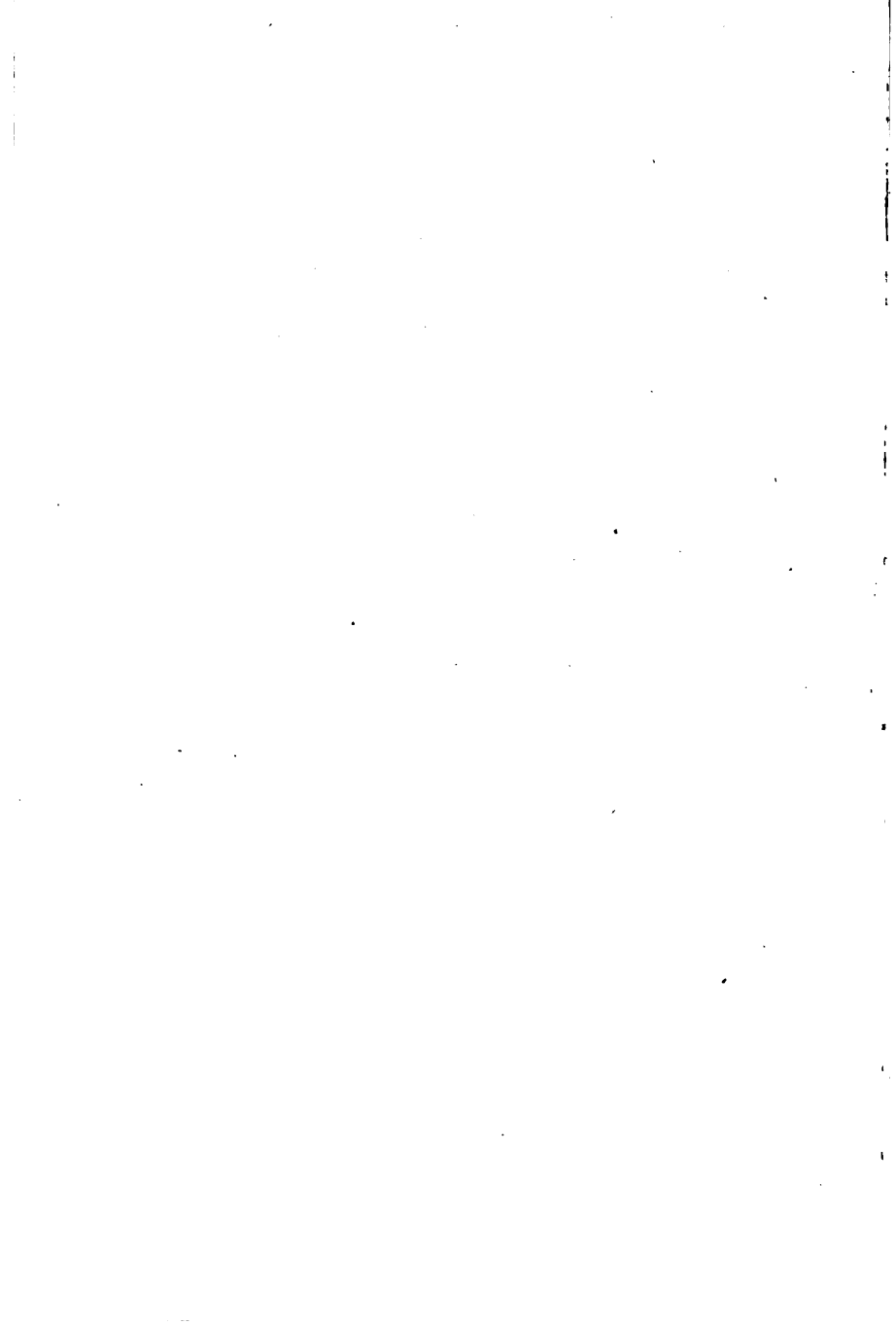
BRIEFER COURSE.

ELEMENTS OF CHEMISTRY,

DESCRIPTIVE AND QUALITATIVE.

BY

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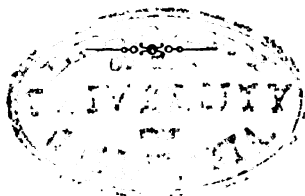
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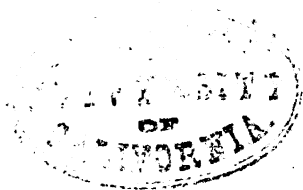
PREFACE.

THIS briefer course follows, in general, the plan of Shepard's Elements of Chemistry; but the reader will notice that the student is told, to a still less extent than in the larger book, what he may expect to see while working.

Directions for preparing reagents, and equipping the laboratory, and discussions of methods of presentation are not given here, since these matters are fully treated in the larger book, which is now so generally used that it is readily accessible to all.

The subject-matter of this text is so arranged, and the experiments are so simplified, that the laboratory work will come within the time available in those schools where but part of the year is allotted to the study of chemistry. The text will also be found acceptable in many schools where a special or a technical course is offered.

Data for chemical computations given at the beginning of the chapters, numerous exercises for review or advanced course, a close adherence to inductive methods, and, wherever possible, careful experimental illustrations

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of all important facts not readily understood by analogy, are features of this briefer course which will, it is hoped, commend themselves to the many truly scientific educators of the youth in all parts of our land.

In the chapters devoted to the carbon compounds, owing to the unsatisfactory results usually to be had at the hands of beginners working with organic substances, it seemed best to limit the work to the preparation and discussion of the more important compounds and at the same time dwelling upon the general laws governing the origin of the derivatives belonging to the different series.

The author takes pleasure in acknowledging the valuable assistance rendered during the preparation of this work by Mr. H. Ellsworth Call, of the Des Moines, Ia., High School; Miss Ada J. Todd, of the Bridgeport, Conn., High School; Mr. H. N. Chute, of the Ann Arbor, Mich., High School; Prof. I. P. Bishop, State Normal and Training School, Buffalo, N. Y.; Mr. J. T. Draper, Pueblo High School, Col.; and by many other prominent educators in all parts of the country.

<div align="right">J. H. S.</div>

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INTRODUCTION

1. Origin of Chemistry. — The rudiments of the science of Chemistry may be traced back to the ancient Egyptians.

About 640 A.D. the Arabs invaded Egypt, where they obtained a knowledge of the sciences practised there. During the Middle Ages they preserved this knowledge, and from their academies in Spain as centres, it gradually spread over all parts of the civilized world. Up to this time the main inducement for studying and practising chemistry was a hope of discovering the Philosopher's Stone, a stone that should change the baser metals into gold. During these researches many important facts in inorganic chemistry were discovered.

From the fifteenth to the seventeenth century the *Elixir Vitæ*, or Elixir of Life, a cordial that should cure all the ills of mankind and give perpetual youth, was the chief object sought. In this search many valuable medicines were discovered.

During the seventeenth century the properties of gases were investigated, and in both this and the succeeding century other important advances were made.

Notwithstanding all previous advancement, however, the modern science of Chemistry is emphatically a product of the present century.

2. Experimentation. — The greatest hindrance to chemical progress in the past lay in the fact that the science of ex-

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perimenting was not well understood. Erroneous theories were advanced and believed in for centuries. These theories were finally overthrown by the rigid test of experiment, and thus progress and improvement were made possible.

When we *experiment* with a substance, we so treat it that we may ascertain its properties and behavior.

In experimenting with substances, the chemist finds frequent use for such processes as Solution, Evaporation, Precipitation, Filtration, Decantation, Reduction, Distillation, and Electrolysis. Excepting the two latter, which will be explained hereafter, these processes may be illustrated by experiments.

3. Solution. — EXPERIMENT 1. Place about a gram of common salt (NaCl) in a test-tube, and then fill the test-tube half full of water. Now gently heat the tube in the Bunsen flame (Fig. 1); frequently cover the mouth of the tube with the thumb and shake.
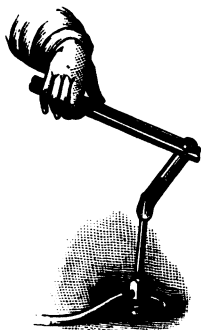
EXERCISE. What becomes of the salt? Define the process called "solution." What is a solution? Define solids; liquids; gases.

4. Evaporation. — EXP. 2. Place a few drops of the salt solution obtained in Exp. 1 on a piece of tin or in an iron spoon. Now warm gently till the water has disappeared.

FIG. 1.

Ex. What became of the water? What remains on the tin? Define evaporation. What is the object of evaporation?

5. Precipitation. — EXP. 3. To about one-half of the salt solution (Exp. 1) add nearly an equal volume of a solution of silver nitrate ($AgNO_3$).

Ex. What takes place? (The silver of the silver nitrate has united with the chlorine of the common salt to form the solid silver chloride, AgCl, thus removing the chlorine from the salt solution, or the silver from the silver nitrate solution.) What is the object of precipitation? Why would not evaporation do instead? Define precipitation; precipitate.

6. Filtration. — EXP. 4. Support a funnel on a ring-stand, and place a beaker underneath the funnel; fold a round filter-paper twice (Fig. 2), making the folds at right angles to each other; place the point of the paper in the funnel, and open one of the pockets formed by folding the paper: into this pocket pour the contents of the tube used in Exp. 3.
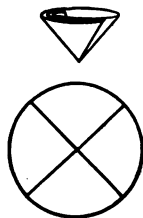
FIG. 2.

Ex. What occurs? What is the object of filtration? Would evaporation have answered as well? Try it. Define filtration; filtrate. How can you wash the precipitate while it is on the filter-paper?

7. Decantation. — EXP. 5. Precipitate the remainder of the salt solution (Exp. 1) with silver nitrate; warm gently, and allow the tube to stand for a few minutes. Now pour off the solution, leaving the solid precipitate in the tube.

Ex. What have you accomplished? Define decantation. How can you wash a precipitate by decantation? Compare decantation with filtration.

8. Reduction. — EXP. 6. Into a piece of charcoal bore a hole with the point of a penknife, and in this hole place the precipitate obtained in Exps. 4 or 5. Now heat this precipitate in the blow-pipe flame (Fig. 3).
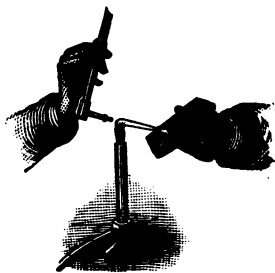
FIG. 3.

Ex. What is the bead you thus obtain? What became of the chlorein? What does "reduction" mean?

9. Elements. — In the last experiment silver was obtained from a substance that did not at all resemble silver. In fact, silver was reduced from its chlorine compound. Chemists have found, however, that neither the silver nor the chlorine can be further divided; hence these substances are called elements.

DEFINITION. A chemical element is a substance that cannot be divided, or at least has not been divided, into simpler substances.

At the present time about seventy different elements are known. Of course it has not been possible to examine every portion of the earth's crust for elements, but such elements as are now discovered from time to time occur only in very small quantities.

Again, it is possible that some substances now known to us as elements may prove to be compounds as our appliances for chemical investigation are improved.

The following table gives a list of the elements. The first column contains the names of the elements; the signification of the other columns will be explained further on.

10. A Table of the Elements.

Names.	Symbols.	Atomic Weights.	Physical condition at ordinary temperature.	Specific Gravity.
Aluminum	Al''''	27.	Solid	2.60
Antimony	Sb''',ᵛ	120.	"	6.71
Arsenic	As''',ᵛ	75.	"	5.73
Barium	Ba''	137.	"	3.75
Beryllium	Be''	9.	"	2.07
Bismuth	Bi''',ᵛ	208.	"	9.80
Boron	B'''	11.	"	2.5?
Bromine	Br',ᵛ	80.	Liquid	3.187
Cadmium	Cd''	112.	Solid	8.60
Caesium	Cs'	133.	"	1.88
Calcium	Ca''	40.	"	1.57
Carbon	C''''	12.	"	3.5–.6
Cerium	Ce''',''''	141.	"	6.68
Chlorine	Cl',ᵛ	35.5	Gas	2.450
Chromium	Cr'''', ᵛⁱ	52.	Solid	6.50
Cobalt	Co'',''''	59.	"	8.5–.7
Copper	Cu''	63.3	"	8.95
Didymium	D'''	142.3	"	6.54
Erbium	E'''	166.	"	—
Fluorine	F'	19.	Gas	1.313
Gallium	G''''	69.	Solid	5.95
Gold	Au',''''	196.5	"	19.32
Hydrogen	H'	1.	Gas	0.069
Indium	In''''	113.6	Solid	7.42
Iodine	I',ᵛ	127.	"	4.948
Iridium	Ir'','''',ᵛⁱ	193.	"	22.42
Iron	Fe'','''',ᵛⁱ	56.	"	7.86
Lanthanum	La'''	138.2	"	6.10
Lead	Pb'',''''	207.	"	11.37
Lithium	Li'	7.	"	0.59
Magnesium	Mg'','''',ᵛⁱ	24.	"	1.74
Manganese	Mn''	55.	"	8.03
Mercury	Hg''	200.	Liquid	13.55
Molybdenum	Mo'','''',ᵛⁱ	96.	Solid	8.60
Nickel	Ni'',''''	58.	"	8.90

Names.	Symbols.	Atomic Weights.	Physical condition at ordinary temperature.	Specific Gravity.
Niobium	Nb^v	94.	Solid	7.06
Nitrogen	N^{III,v}	14.	Gas	0.971
Osmium	Os^{II,IIII,vi}	199.	Solid	22.48
Oxygen	O^{II}	16.	Gas	1.105
Palladium	Pd^{II,IIII}	106.	Solid	11.40
Phosphorus	P^{I,III,v}	31.	"	Colorless 1.83 Red 2.20
Platinum	Pt^{II,IIII}	195.	"	21.50
Potassium	K^I	39.	"	0.87
Rhodium	Ro^{II,IIII,vi}	104.	"	12.10
Rubidium	Rb^I	85.	"	1.52
Ruthenium	Ru^{II,IIII,vi}	103.5	"	12.26
Samarium	Sm	150.	"	—
Scandium	Sc	44.	"	—
Selenium	Se^{II,IIII,vi}	79.	"	4.50
Silicon	Si^{IIII}	28.	"	2.39
Silver	Ag^I	108.	"	10.53
Sodium	Na^I	23.	"	0.978
Strontium	Sr^{II}	87.5	"	2.54
Sulphur	S^{II,IIII,vi}	32.	"	2.05
Tantalum	Ta^v	182.	"	10.40
Tellurium	Te^{II,IIII,vi}	125.?	"	6.40
Terbium	Tb	148.5?	"	—
Thallium	Tl^{I,III}	204.	"	11.85
Thorium	Th^{IIII}	232.	"	11.00
Tin	Sn^{II,IIII}	118.	"	7.29
Titanium	Ti^{II,IIII}	48.	"	—
Tungsten	W^{IIII,vi}	184.	"	19.12
Uranium	U^{IIII,vi}	239.8	"	18.70
Vanadium	V^{III,v}	51.5	"	5.50
Ytterbium	Yb	173.	"	—
Yttrium	Y^{III}	89.	"	—
Zinc	Zn^{II}	65.	"	7.15
Zirconium	Zr^{IIII}	90.	"	4.15

11. Atoms. — It is the prevailing belief that matter is made up of extremely minute, indivisible particles called atoms. Many reasons lead to the conclusion that all the atoms of the same element are alike, but that they are unlike the atoms of any other element.

12. Symbols. — It is often convenient to represent the name of an element by some letter or letters, as H for hydrogen, O for oxygen, Cd for cadmium, etc. In the second column of the table (Art. 10) are given the symbols commonly employed. These symbols are also used for other purposes, thus: H also stands for an atom of hydrogen, O for an atom of oxygen, etc. When we wish to represent more than one atom, figures are used, thus: 2 H means two atoms of hydrogen; 3 H, three atoms; etc. Subscript figures are used for the same purpose when more than one symbol is needed to represent certain substances; thus: H_2O, water; NH_3, ammonia; C_2H_4, ethylene; etc.

Some elements have symbols derived from their Latin names. This is perplexing to the student, but this list will explain : —

Antimony,	Sb,	from	Stibium.
Copper,	Cu,	"	Cuprum.
Gold,	Au,	"	Aurum.
Iron,	Fe,	"	Ferrum.
Lead,	Pb,	"	Plumbum.
Mercury,	Hg,	"	Hydrargyrum.
Potassium,	K,	from	Kalium.
Silver,	Ag,	"	Argentum.
Sodium,	Na,	"	Natrium.
Tin,	Sn,	"	Stannum.
Tungsten,	W,	"	Wolframium.

NOTE. At the right of the symbols in the table the indices and numerals are used to indicate the valence (Art. 76) of the elements. The symbols are commonly written without these.

13. Compounds. — EXP. 7. Mix thoroughly 0.56^g very fine iron filings and 0.32^g flowers of sulphur. Place this mixture

in an iron spoon, and heat it to redness in the Bunsen flame. The iron and sulphur combine, forming the chemical compound, ferrous sulphide (FeS).

Ex. Define a chemical compound. Compare the ferrous sulphide with the iron and sulphur of which it is composed.

14. Law of Definite Proportions. — When elements unite, as in the case of iron and sulphur, it has been proven that they always unite in fixed and definite proportions. For example: 56 parts, by weight, of iron always unite with 32 parts of sulphur, to form ferrous sulphide (FeS). Again: 23 parts of sodium always unite with 35.5 parts of chlorine to form common salt (NaCl), etc. The law may be stated in this form: —

Any given chemical compound always contains the same elements in the same proportions by weight.

15. Atomic Theory. — To account for the union of elements in definite proportions by weight, the supposition has been made that the atoms of the elements are the units between which the union takes place.

The simplest case is where one atom of one element unites with one atom of another, as in common salt (NaCl), where one atom of sodium unites with one atom of chlorine. The next case is where two atoms of one element unite with one atom of another, as in water (H_2O), where two atoms of hydrogen unite with one of oxygen. Other relations also exist with which the student will soon become familiar.

16. Atomic Weights. — It is evident that, however small atoms may be, they must still have some weight. It is true that the weight of the heaviest atom is so slight that

it could not be determined by the most delicate balance ever constructed, but it is also true that it is not necessary to know the *absolute* weights of the atoms. If we can determine their *relative* weights, all purposes will be sufficiently answered: and this has been done. For this purpose the hydrogen atom has been taken as unity, and the relative weights of the atoms of the other elements, as compared with the hydrogen atom, have been determined. How this has been accomplished will be explained hereafter; for the present it must suffice to say that the atom of oxygen has been estimated to be 16 times as heavy as the hydrogen atom, the atom of iron 56 times as heavy, and the atom of mercury 200 times as heavy; and so, likewise, certain numbers have been assigned to the atoms of all the known elements. Now, these numbers are called the atomic weights of the elements.

Moreover, since these numbers fix the ratios in which the elements combine, they are also called *Combining Numbers*; *e.g.* 56 and 32 are respectively the combining numbers of iron and sulphur. The atomic weights now assigned to the elements are given in the third column of Art. 10.

17. Molecules. — We have already learned (Exp. 3) that the atoms of silver unite with the atoms of chlorine to form silver chloride. If we consider a quantity of silver chloride containing but one atom each of silver and chlorine, it is evident that no smaller quantity of silver chloride could exist, since the atoms themselves are indivisible; and if we take away, for example, the atom of chlorine, free silver is obtained (Exp. 6). To such a smallest possible quantity of a chemical compound that can exist as such the term *Molecule* is applied.

18. Molecular Formulæ. — In representing the molecules of compound bodies, the symbols of the elements composing those bodies are written side by side, thus: silver nitrate, $AgNO_3$; sulphuric acid, H_2SO_4; potassium nitrate, KNO_3; etc. If we wish to write any number of molecules of a substance, figures are used: thus, $3 KNO_3$ means three molecules of potassium nitrate; $2 H_2O$, two molecules of water; etc.

In the case of the molecules of the elements it is customary to write the number of atoms in the molecule by means of a subscript figure: thus, H_2, O_2, N_2, etc., represent molecules.

NOTE. It has been a very difficult task to determine the molecular formulæ of the compounds. How this may be done will be explained in a subsequent chapter.

EX. Determine the number of oxygen atoms represented in the following: $3 H_2SO_4$; $8 HNO_3$; $16 K_2Cr_2O_7$; $24 H_2O$; $5 Ca(NO_3)_2$.

19. Chemism, or Chemical Affinity. — The force causing atoms to unite with one another to form molecules is called *Chemism*. Between the atoms of any two elements this force is always a constant quantity; but it varies for the atoms of any other element when taken with either of these two elements.

EXERCISES.

(For Review or Advanced Course.)

1. Attach threads to the four corners of a small square of wire gauze, and then place on the gauze a crystal of copper sulphate, $CuSO_4$. Now suspend the crystal on the gauze in a beaker of water. Note the phenomenon of solution.

2. Will alcohol dissolve in water? Will sulphuric acid? Will oil? Will camphor gum dissolve in water? in alcohol? What will dissolve rubber gum?

3. Place a beaker of fresh well-water in a warm place, and allow it to remain quiet for some time. What collects on the sides of the glass? Is

air soluble in water? Is ammonia gas? Name some other gases that are soluble in water.

4. Define a solvent; a menstruum; a tincture; a fluid extract; a saturated solution; a dilute solution.

5. Carefully weigh an evaporating-dish, and then place in it exactly 0.65g zinc. Place the evaporating-dish on the sand-bath, and cover the zinc with hydrochloric acid, HCl. Heat the sand-bath gently, and add more hydrochloric acid, if necessary, till the zinc is all dissolved. You thus obtain a solution of zinc chloride, $ZnCl_2$. Now carefully evaporate this solution to dryness, and then place the evaporating-dish under a small bell-glass till the dish and its contents are cool. Rapidly weigh the dish and its contents, and from this weight subtract the weight of the dish. This gives the weight of the zinc chloride. From this last weight subtract the weight of the zinc, and thus obtain the weight of the chlorine that united with the zinc.

From the formula $ZnCl_2$ it appears that 0.71 parts of chlorine should unite with 0.65 parts of zinc; hence the zinc chloride should weigh 0.65g + 0.71g = 1.36g. What does this experiment show?

NOTE. Owing to experimental errors and to the influence of moisture, these results will only be approximated.

6. Moisten with water a pine splinter or a partly burned match, and dip it into dry powdered sodium carbonate, Na_2CO_3. Heat the match in the Bunsen flame till dry and charred. If the match be not coated with the carbonate, moisten, and proceed as before. With the warm match take up a small bit of silver chloride (Exp. 3), which is to be heated in the Bunsen flame.

Do you thus obtain a bead? Compare with Exp. 6. Try in this way some compounds of lead and copper.

CHAPTER I.

OXYGEN.

DATA FOR COMPUTATIONS. — Symbol, O ; Molecular Formula, O_2 ; Atomic Weight, 16 ; Specific Gravity, 1.1056 ; Weight of 1^l at 0° C. and 760^{mm}, 1.430^g.

20. Occurrence. — Oxygen is the most abundant of all the elements. It occurs free in the atmosphere, of which it constitutes about 23 per cent by weight. In its compounds oxygen occurs most plentifully, since from 44 to 48 per cent by weight of the earth's crust, and 88 to 89 per cent by weight of water, consists of oxygen. Every element except fluorine unites with oxygen to form compounds.

21. Preparation and Properties. — Since oxygen occurs free in the atmosphere, we have all had some experience with it in that form. As it thus occurs it is largely diluted with nitrogen and other gases. Notwithstanding our familiarity with atmospheric oxygen, it will be well, in this connection, to make one or two experiments.

EXP. 8. Ignite a common match, and when burning freely hold the tip upward. Note the flame, and how the match is consumed. When a portion of the match is charred, extinguish the flame, and note the behavior of the glowing coal which remains.

EXP. 9. Cease breathing for about fifteen seconds, and note the effect upon the system.

Ex. When the flame is extinguished, does the match still continue to waste away? How does the flame differ from the slow burning of the

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coal ? What remains after the charcoal has burned away ? Is wood an element or a compound ? For how long a time would it be safe to "hold the breath " ? Define suffocation ; strangulation ; asphyxiation.

The two great uses of free atmospheric oxygen are to support respiration and combustion.

All animals consume free oxygen during respiration. In the case of air-breathing animals the blood, while passing through the lungs, is thoroughly brought into contact with the air; and thus is the blood purified. In water-breathing animals, like fishes, gills take the place of lungs; while in the still lower orders, pores and spiracles, distributed over the surface of the body, serve a like purpose.

When we say a body burns, it is equivalent to saying that it unites with oxygen. In fact, when wood, coal, gas, oils, etc., are burning, these substances are entering into chemical combination with the oxygen of the air. A flame is a burning gas; hence solids must be heated to a temperature (the kindling-point) high enough to convert them into gases before flames are produced. Substances may oxidize or burn at high or low temperatures. When flames are produced, the temperature is high; but when iron is rusting, or wood rotting, or oxygen combining with the impurities of the blood, the temperature is low. It matters not, however, at what temperature the oxidation may occur; a given weight of a substance, when oxidized, always produces the same quantity of heat.

Ex. Define combustion ; oxidation. Why can a lump of coal not be ignited by means of a match ? Explain the philosophy of "kindling-wood." Why does blowing a fire hasten combustion, while the same treatment would extinguish a candle flame ? Explain the use of chimneys, drafts, and dampers in stoves and furnaces.

Pure oxygen varies much from the diluted gas in the phenomena which it exhibits during combustion. There

are several ways of preparing pure oxygen, but the best
ones are by decomposing its compounds, such as red oxide
of mercury or mercuric oxide, HgO, and potassium chlo-
rate, $KClO_3$, by means of heat.

Exp. 10.   Place a small quantity of mercuric oxide in a test-
tube.   Heat the test-tube just under the oxide in the Bunsen
flame for a short time, frequently inserting a glowing match.

Ex.   Compare with Exp. 8.   What collects on the sides of the tube?
Into what substances has the oxide of mercury been separated?   Has
oxygen an odor? any color?   Why are these two latter facts wise
provisions?

This method of preparing oxygen would be too expensive
when large quantities of that gas are needed for laboratory
purposes.   In the latter case potassium chlorate is used.
In order to have the gas liberated at as low a temperature
as possible, one-fourth part, by weight, of black oxide of
manganese or manganese dioxide, MnO_2, is mixed with
the potassium chlorate.   The manganese dioxide under-
goes no change, but the potassium chlorate is reduced to
potassium chloride, KCl.

Exp. 11.   Place a small quantity of this mixture in a test-
tube, and proceed as in Exp. 10.   Compare the results with
that experiment.

Exp. 12.   Place (say) 100ᵍ potassium chlorate and 25ᵍ man-
ganese dioxide in an oxygen generator.   Be *sure* that the
chemicals are pure.   Heat carefully, and collect the gas in
gas-bags or in jars over the pneumatic trough, or in gas-
holders.   Now prepare the materials for the following exper-
iments, which are best shown in a darkened room.

Exp. 13.   Make a pencil of bark charcoal, and tie around
it an iron wire.   Ignite the charcoal, and by means of the
wire lower it into a jar of oxygen.   Note the scintillations.

Exp. 14. Draw the temper from a watch-spring by heating it in the Bunsen flame, and uncoil it. File one end thin, and bend it into a loop. Now heat the loop, and make a sulphur tip for the spring by dipping the heated loop into flowers of sulphur. Ignite the sulphur, and carefully place the spring in a jar of oxygen. Note the sulphur flame and the combustion of the spring (Fig. 4).

Exp. 15. Make a small pencil by twisting together fine iron wires; tip it with sulphur, and proceed as in the last experiment.

NOTE. A large bottle with its bottom removed, and resting on a dinner-plate containing water, makes a good and cheap apparatus for the last three experiments; and it will also answer for the next experiment if no globe be at hand.

FIG. 4

Exp. 16. Place a bit of dry phosphorus as large as a pea in a deflagrating-spoon, always remembering to handle the phosphorus with pincers, and not with the fingers; ignite the phosphorus, and lower it into a globe of oxygen gas. Note the color of the flame. This experiment produces what is known as the "Phosphorus Sun."

Ex. All these experiments furnish examples of what? Write a short description of each experiment. Why do these phenomena not occur in atmospheric oxygen? Enumerate the properties of oxygen.

22. Crystallization. — Exp. 17. Place the residue remaining in the oxygen generator (Exp. 15) in a large beaker-glass, and add about a litre of hot distilled water. Agitate the con-

tents of the beaker with a glass rod until the lumps have all disappeared; the potassium chloride is now dissolved, while the manganese dioxide is unaltered. Pour the contents of the beaker on a large filter-paper fitted to an appropriate funnel, and receive the filtrate in a large evaporating-dish. Now evaporate the contents of the dish down to less than $\frac{1}{4}$, and then set the dish away to cool, leaving it for several hours undisturbed. Crystals of potassium chloride will form in the dish. These crystals may be removed from the solution by filtering through a fresh filter-paper; and they may be dried by simply allowing them to remain on the filter-paper, exposed to the air. A second crop of crystals may be had by concentrating the remaining solution ("mother liquor"), and cooling as before.

NOTE. The manganese dioxide may be dried on the filter-paper and put away for future use.

Ex. What processes were employed in obtaining the crystals? Define crystallization; "mother liquor"; a crystal.

23. Ozone. — Oxygen exists in a peculiarly modified and unstable form called *ozone*. In this form three volumes of ordinary oxygen are condensed to two volumes; accordingly the formula of its molecule is written O_3.

Ozone occurs free in the atmosphere in minute quantities, probably being produced through the agency of electricity and by the vaporization and condensation of atmospheric moisture.

Exp. 18. Fill a test-tube about one-third full of a saturated solution of potassium permanganate, $K_2Mn_2O_8$, and then cautiously add a few drops of sulphuric acid, H_2SO_4. Test the escaping gas by a glowing match. Note the odor. Suspend in the tube a strip of paper moistened in a solution of starch paste and potassium iodide, K.

Ex. Compare ozone with pure oxygen.

Ozone is much more energetic in its action than the ordinary oxygen, and especially is this held to be true concerning its action upon organic matter and noxious exhalations from unhealthy localities. It is also believed that ozone is capable of destroying many kinds of disease germs.

24. Tests for Oxygen and Ozone. — 1. Free oxygen gas is detected by its lack of odor, taken together with its action upon a glowing match. If the gas be dilute, the coal barely continues to glow; but if pure, the match bursts into flame.

2. Ozone is detected by its odor, by its kindling a glowing match, and by its coloring blue a strip of paper moistened in a solution of starch paste and potassium iodide.

EXERCISES.

(For Review or Advanced Course.)

1. The molecular weight of a compound substance is equal to the sum of the atomic weights of the elements forming that substance. Compute the molecular weights of the following: HgO; $KClO_3$; KCl; H_2SO_4; $AgNO_3$.

2. How much oxygen is there in 100g HgO?

SUGGESTION. The molecular weight of HgO is $(Hg) 200 + (O) 16 = 216$. Now $\frac{16}{216}$ of any weight of HgO is oxygen.

3. How many litres of oxygen at $0°$ C. and 760^{mm} are there in 484g of oxygen? See data for computations.

4. How many litres of oxygen at $0°$ C. and 760^{mm} may be had from 150g $KClO_3$?

5. How many pounds of oxygen are there above one square foot of the earth's surface at the level of the sea?

SUG. At the sea-level the atmosphere weighs about fifteen pounds to the square inch.

6. Hold a short piece of stick phosphorus by means of a pair of pincers, and scrape it clean under water. Loop a thread around the phosphorus, and suspend it in a bottle containing a few drops of water. Set

the bottle in a moderately cool place ($15°$ to $20°$ C.). Now suspend in the bottle a strip of paper prepared for testing ozone. Note from time to time the color of the paper.

7. Set a Toepler-Holtz machine in motion, and after a few sparks have passed, note the odor. Test the vicinity of the poles with ozone paper.

8. Explain the construction of the Bunsen burner. Why is the Bunsen flame colorless ?

9. Examine the blow-pipe flame. Note the inner bluish cone and the outer slightly luminous layer. This latter portion of the flame contains an excess of oxygen, heated to a very high temperature. Substances placed in this part of the flame are oxidized, hence the name *Oxidizing* flame. The best place to hold a substance to be oxidized is just beyond the bluish tip.

The central part of the flame contains an excess of highly heated carbon and hydrogen, and substances placed within the cone loose their oxygen or are reduced, hence the name *Reducing* flame.

10. Bend a small loop on a piece of platinum wire. Heat the loop, and dip it into powdered borax. Fuse the borax on the wire to a colorless bead. Now *slightly* moisten the bead with ferrous sulphate, $FeSO_4$, and heat it in the oxidizing flame. The bead becomes reddish in color when hot, light yellow when cold. Again heat this bead in the reducing flame ; it becomes colorless. Why ?

CHAPTER II.

HYDROGEN AND ITS OXYGEN COMPOUNDS.

DATA FOR COMPUTATIONS. — Symbol, H ; Molecular Formula, H_2 ; Atomic Weight, 1 ; Specific Gravity, 0.0692 ; Weight of 1^l at 0° C. and 760^{mm}, 0.0896^g.

25. Occurrence. — Free hydrogen occurs only in insignificant quantities, being found chiefly in volcanic gases. In its compounds, however, hydrogen occurs plentifully. Thus, of water, H_2O, it constitutes 11.1 per cent by weight; while it is always present in ammonia, acids, and organic compounds.

26. Preparation and Properties. — Hydrogen is readily obtained from its compounds, such as water, H_2O, and from acids, such as hydrochloric acid, HCl, and sulphuric acid, H_2SO_4.

EXP. 19. Place about 5^g mercury in a porcelain mortar; on the mercury place about 0.5^g metallic sodium. Now, by means of a pestle, bear the sodium down through the mercury to the bottom of the mortar, and then twist the pestle till the sodium and mercury unite to form an amalgam.

Fill a test-tube half full of water, and into this drop a piece of the amalgam. Note the bubbles of gas escaping, and note their color and odor, if any. Hold the tube firmly, and carefully bring a lighted match near its mouth.

Ex. What became of the mercury used in making the amalgam ? Rub some of the water in the test-tube between the thumb and finger, and note the feeling. Has the water changed ? Dip a strip of red litmus

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paper in the water, and note the change in the color of the paper. Is an alkali present? (SUG. Alkalies turn red litmus paper blue.) Is hydrogen inflammable? Has it an odor or a color? Define an amalgam.

In this experiment hydrogen was obtained from water. One atom of sodium displaced or set free one atom of hydrogen, and formed the alkali, caustic soda, or sodium hydroxide. The reaction — that is, the changes that took place — can best be shown by means of an

EQUATION. Thus, $Na + H_2O = NaOH + H$. This equation is read, "Sodium and water give sodium hydroxide and hydrogen." Equations are further useful, since they enable us to tell what proportions, by weight, of substances take part in chemical reactions. This is accomplished by means of the weights of the atoms and of the molecules represented in the equation. For example, $23 (Na) + 18 (H_2O) = 40 (NaOH) + 1 (H)$. That is, 23 parts, by weight, of sodium react with 18 parts of water to give 40 parts of sodium hydroxide and 1 part of hydrogen.

FIG. 5.

Ex. Explain these equations:

HgO (heated) $= Hg + O$,

and

$KClO_3$ (heated) $= KCl + 3 O$.
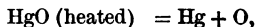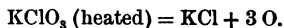
EXP. 20. Arrange a jar filled with water, as in Fig. 5. Wrap a piece of sodium amalgam in wire gauze, and place it under the mouth of the jar. Hydrogen rises in the jar. Test the gas by raising the jar, mouth downwards, and thrusting a lighted taper up into the jar. The hydrogen will burn around the mouth of the jar, while the taper will be extinguished. The taper may be relighted in the burning gas. A slight but harmless explosion usually terminates the experiment.
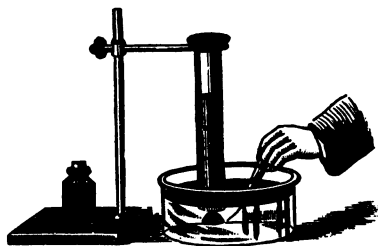
EXP. 21. Half fill an evaporating-dish with warm water, and then drop in a small piece of pure metallic sodium (Fig. 6). Also try in this way a small piece of metallic potassium.

NOTE.   This experiment may terminate with a slight explosion.

Ex.   What advantage is gained by using sodium or potassium amal-
gam ?   Is the water in the evaporat-
ing-dish alkaline after adding the
metals ?   Write the equation for the
reaction between K and H_2O.

Exp. 22.   Fit a cork with a
straight-jet delivery-tube to a
generating-flask.   In the flask
place (say) 10^g granulated zinc.

FIG. 6.

Now fill the flask one-third full of dilute sulphuric acid, made
by adding one part of acid to five parts of water.   Place the
cork and jet in position, and when the air is expelled from the
apparatus, light the jet of escaping gas.   Note the color of
the flame.   Hold a piece of small iron wire in the flame.   Ex-
tinguish the flame, and collect the gas in a gas-bag.

NOTE.   In case the gas is not given off freely, add to the contents of
the flask a few nails or a few small crystals of copper sulphate.

In this experiment the hydrogen is obtained from sul-
phuric acid by means of a reaction with zinc, thus, —

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
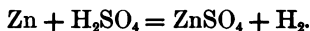
No note is taken of the water added, since this merely
serves to dissolve the zinc sulphate, $ZnSO_4$, as fast as that
salt is formed.

Ex.   What is the color of the hydrogen flame ?   Has the flame a high
temperature ?   By means of a rubber tube fit a common clay pipe to the
gas-bag filled with hydrogen, and blow a few hydrogen soap-bubbles.   Is
hydrogen lighter than air ?   Touch a bubble with a candle-flame.   Write
the equation for Exercise 5 at the close of the Introduction, where zinc
and hydrochloric acid react.

Exp. 23.   Fire the hydrogen pistol to illustrate the explo-
siveness of a mixture of hydrogen and oxygen.

Exp. 24.   Fill a collodion balloon with hydrogen gas, and
then release the balloon in the laboratory.   After some hours

the balloon will settle to the floor. When this has occurred, test the gas in the balloon for hydrogen.

Some or all of the hydrogen in the balloon has passed out into the air through the pores of the balloon, and air has entered through the same channels. This illustrates what is termed *Diffusion* of gases through porous partitions. It is in this way that oxygen passes through the delicate membranes of the pulmonary capillaries to purify the blood in its passage through the lungs.
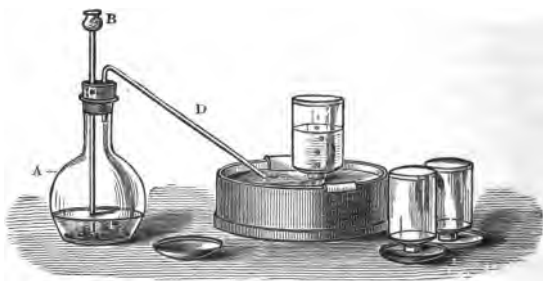
Fig. 7.

Exp. 25. Arrange a delivery-tube for a hydrogen apparatus, as shown in Fig. 7. Using the same materials as in Exp. 22, fill a jar with hydrogen. Then carefully lift up the jar, keeping its mouth downwards. Now slowly bring the mouth of the jar upward, underneath the mouth of a second jar, held mouth downward. When the first jar has reached an upright position, remove it, and test its contents for hydrogen. Also test the contents of the second jar for the same gas.

Ex. What has occurred? Enumerate the properties of hydrogen.

27. Test for Hydrogen. — Hydrogen may be detected by its flame and by its behavior, as in the preceding experiments.

COMPOUNDS OF HYDROGEN WITH OXYGEN.

28. Hydrogen and oxygen unite to form but two chemical compounds: water, H_2O; and hydrogen dioxide, H_2O_2. Of these compounds, water is by far the most important.

WATER.

29. Occurrence. — Water occurs widely distributed in nature. Permeating the atmosphere and soil, flowing in streams and forming lakes and oceans, water is everywhere found. Although the properties of water are familiar to all, nevertheless, since this is the first chemical compound to be studied in detail, it will be necessary to make a few experiments illustrating some of the methods employed by chemists in investigating the composition and properties of bodies.

30. Preparation and Properties. — Let us first make a *qualitative* experiment in order to learn if water can be produced *synthetically*.

EXP. 26. Arrange an apparatus as shown in Fig. 8. G is a hydrogen generator, containing zinc and dilute sulphuric acid. B is a drying-bulb, containing granulated calcium chloride, $CaCl_2$.

FIG. 8.

Introduce the acid through the funnel-tube, and when the apparatus is free from air, ignite the hydrogen gas escaping through the jet, and place the bell-jar, R, over the flame. Note what collects on the sides of the jar.
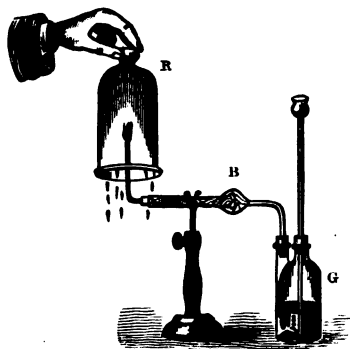
Ex.   Why, in this experiment, should the hydrogen gas be perfectly dry ?   When the hydrogen is burning, with what constituent of the air does it unite ?   What substances, then, enter into the composition of water ?

Next let us make a *quantitative* experiment to determine synthetically in what proportions, by volume, hydrogen and oxygen unite to form water.   This may be accomplished by means of the apparatus (Ure's eudiometer) shown in Fig. 9.

Exp. 27.   The graduated limb and a part of the plain limb are to be filled with mercury.   Then, by means of a curved glass tube, 10 divisions of the graduated limb are filled with pure oxygen; 25 divisions of pure hydrogen are next to be added.   Now bring the mercury to the same level in both limbs, and while firmly holding the thumb over the plain limb, pass an electric spark through the wires attached to the graduated limb.   20 divisions of hydrogen will unite with 10 divisions of oxygen to form water.   It thus appears that these gases unite in the proportion of 2 volumes of hydrogen to 1 volume of oxygen.
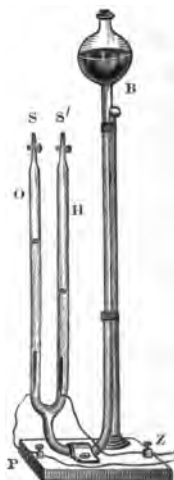
Fig. 9.

Fig. 10.

These two experiments illustrate how the composition of certain bodies may be determined by *Synthesis*.   Another and more extensively employed method is termed *Analysis*.   In the case of water, the analysis may be made by a process termed *Electrolysis*.   The apparatus (Hoffmann's apparatus) used is shown in Fig. 10.

EXP. 28. Add one part, by weight, of sulphuric acid to 20 parts of distilled water. Open the stop-cocks S and S', and then pour the acidulated water into the tube B until it issues from the tubes O and H. Close the stop-cocks, and fill B up to the bulb. Connect the platinum wire Z, which is melted through the tube H and terminates in a platinum strip, with the zinc pole of a Grove's battery, consisting of five or six cells. Also connect the platinum wire P (which is like Z in every respect) to the platinum pole of the battery. Hydrogen collects in the tube H, and oxygen in the tube O. Note the comparative volumes of the gases collected.

The hydrogen may be tested by slightly opening the stop-cock S' and igniting the escaping gas. Open the stop-cock S, and test the oxygen by means of a glowing match.

Ex. What relative volumes of hydrogen and oxygen were liberated ? Compare the results of this experiment with those obtained in Exp. 27. Define synthesis; analysis; a qualitative experiment; a quantitative experiment; qualitative analysis; quantitative analysis; electrolysis; an electrolyte.

The *proportions, by weight*, in which oxygen and hydrogen unite to form water may now be determined.

The preceding experiments show conclusively that in water 2 volumes of hydrogen are united with 1 volume of oxygen. Now let us assign some absolute value to each volume, so that the weights of the volumes may be determined. For example: take 2^l of hydrogen and 1^l of oxygen; then, multiplying the number of litres of each gas by the weight of 1^l of that gas, the proportion, by weight, becomes $2 \times 0.0896 : 1 \times 1.430$ or $0.1792 : 1.430$. This ratio reduced to its lowest terms becomes very nearly $1 : 8$; *i.e.* 1 part, by weight, of hydrogen unites with 8 parts, by weight, of oxygen.

One way of determining the *molecular formula* of water is as follows : —

It must be remembered that the symbols of the elements represent both atoms and the weights of the atoms. Now, since the atomic weight of oxygen is 16, the ratio of $1 : 8$ would only require $\frac{1}{2}$ an atom of oxygen to 1 atom of hydrogen, which is not supposable; but if we multiply the ratio by 2, it becomes $2 : 16$, or 2 atoms of hydrogen to 1 of oxygen. Now these are the fewest number of atoms that could possibly form water. Moreover, experiment has shown that the molecular weight of water is 18. Hence there is but one conclusion: no larger number of atoms enter into the molecule, and water is H_2O. How molecular weights are determined will be explained hereafter.

The *solvent action* of water upon many substances is well understood. Sugar, salt, and similar substances, as well as many liquids and gases, are readily soluble in water. But the solvent powers of water are greater than superficial observation would indicate.

Exp. 29. Place a few clean pine shavings in an evaporating-dish half full of ordinary well water. Boil the contents of the dish for a short time, and then filter. Note the taste and odor of the filtrate

Ex. Has the water dissolved a portion of the pine? What makes water that has stood in wooden pails "taste"?

Limestone, or calcium carbonate, $CaCO_3$, and ferrous carbonate, $FeCO_3$, are insoluble in pure water; but in water charged with carbonic acid gas, CO_2, these substances are readily soluble. When the carbonic acid is expelled by boiling, they both become insoluble again and are precipitated. In the case of many other substances, such as certain organic compounds, and metals like lead and copper, impure water will act as a solvent where pure water would have no action.

Exp. 30. Fill a beaker with ordinary well-water. Place the beaker on the sand-bath, and boil the water for a short time. Note any cloudiness or precipitate that may appear in the water.

Ex. Why did the precipitate form ? Why is a crust formed on the inside of a tea-kettle in which hard water is boiled ? Explain the formation of fossils. Knowing that the coloring-matter of vegetation is partly composed of iron, explain why the waters of springs and creeks deriving their supplies from marshy lands contain iron. Why do these waters deposit iron ores ? Explain the formation of sedimentary rocks. How did the deposition of sandstone differ from that of limestone ? Which will dissolve more common salt, hot or cold water ? Why is water flowing through lead pipes dangerous to drink ? Why is drinking-water liable to contain organic matter ? In what ways is water useful to plants and animals ?

Besides acting as a solvent, water fulfils another extremely important office : it acts as a *heat regulator*. In changing 1^{kg} of ice from a solid at $0°$ C. to a liquid at the same temperature, 79 heat-units, or calories, are rendered latent; while into 1^{kg} of water, in passing from a liquid at $100°$ C. to steam at $100°$, 536 calories disappear. When water freezes, or when steam condenses, the latent heat is again given up to the atmosphere or to surrounding objects. Moreover, water receives and parts with its heat very slowly, and thus it modifies climatic extremes.

Water is at its maximum density at $+4°$ C. When its temperature passes either above or below this point, water expands. Consequently, ice is lighter than water; and forming, as it does, at the surface of lakes and rivers, it acts as a protection to the water underneath. Snow serves as a protection to the ground, and clouds prevent a rapid loss of heat by radiation from the surface of the earth.

EXERCISES.

(*For Review or Advanced Course.*)

1. How many litres at 0° C. and 760^{mm} are there in 4.326^g hydrogen ?

2. How many litres of oxygen would be required to form water with the hydrogen in the preceding exercise ? What would the oxygen weigh? How much water would be formed ?
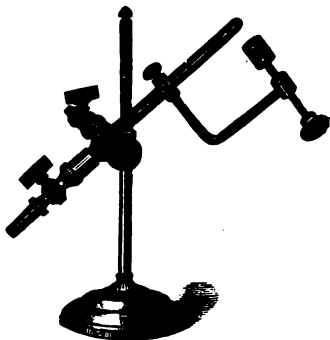
FIG. 11.

3. Bearing in mind that one calorie of heat will raise 1^{kg} of water through 1° C., how many calories would be required to convert 10^{kg} of ice at 0° into steam at 100° ?

4. Name 10 substances that are soluble in water, and 10 that are insoluble.

5. Prepare and test hydrogen dioxide, H_2O_2, thus : Make a mixture of 2^{cc} sulphuric acid and 20^{cc} water. Place the mixture in a beaker, and when cool, add, with constant stirring, 6^g finely pulverized barium dioxide, BaO_2. Filter the contents of the beaker, or allow the white precipitate to subside, thus obtaining a clear solution of hydrogen dioxide : $BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4$. The white precipitate is barium sulphate.

Test the hydrogen dioxide thus: To about a half of a test-tube of the solution add successively 2 or 3 drops of sulphuric acid, 5 or 6 drops of potassium dichromate, $K_2Cr_2O_7$, and about 2^{cc} ether, $(C_2H_5)_2O$. Now shake the tube thoroughly, and note the blue-colored solution obtained.

FIG. 12.

6. Determine the *total residue* in a sample of drinking-water, thus : Weigh an evaporating-dish, and in it carefully evaporate to dryness over a water-bath one-half litre of the sample. Place the dish and its contents over a dish containing strong sulphuric acid, and cover the whole with a small bell-jar. When cool, weigh the dish and its contents ; from this weight subtract that of the dish, and multiply the difference by 2. The result is the total residue per litre sought.

7. Explain the principles involved in the oxyhydrogen blow-pipe (**Fig. 11**). The tip is shown in Fig. 12.

CHAPTER III.

NITROGEN AND ITS COMPOUNDS WITH HYDROGEN AND OXYGEN.

DATA FOR COMPUTATIONS. — Symbol, N ; Molecular Formula, N_2 ; Atomic Weight, 14 ; Specific Gravity, 0.971 ; Weight of 1^l at $0°$ C. and 760^{mm}, 1.256s.

31. Occurrence. — Nitrogen is found free in the atmosphere, of which it constitutes nearly four-fifths part by volume, or 77 per cent by weight. In compounds, nitrogen occurs in such substances as ammonia, NH_3 ; potassium nitrate, or saltpeter, KNO_3 ; sodium nitrate, or Chili saltpeter, $NaNO_3$; and in many organic compounds.

32. Preparation and Properties. — EXP. 31. Float an iron sand-bath or a tin cup on the water of the pneumatic trough, or of any convenient vessel. Into the cup drop a bit of phosphorus. Ignite the phosphorus, and then carefully place down over it a bell-jar (Fig. 13). White fumes of phosphorus pentoxide, P_2O_5,

FIG. 13. .

and perhaps of the trioxide, P_2O_3, quickly fill the jar. These fumes soon subside, and dissolve in the water, leaving the nitrogen nearly pure.
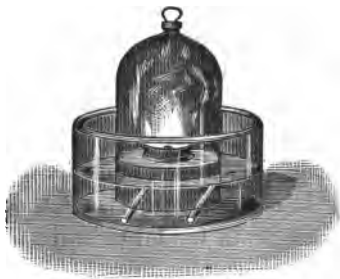
Ex. What substance was removed from the air in the jar by the burning phosphorus? Are the fumes formed solid or gaseous? Why would gaseous products in this experiment be objectionable?

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Exp. 32. Lower a burning taper into a jar of nitrogen. Try a glowing match. Compare the phenomena observed with those obtained in oxygen.

Exp. 33. Place a live mouse in a jar of nitrogen.

Ex. Is nitrogen a supporter of combustion? of life? What purpose does nitrogen serve in the atmosphere? Is nitrogen poisonous? Would a mixture of air and nitrogen explode? Has nitrogen any color or odor? Enumerate the properties of nitrogen.

Nitrogen possesses a very feeble chemism for the other elements, in consequence of which it does not enter directly into combination with them. Indirectly, however, it forms many important compounds, as will appear further on. Owing to its passive nature, nitrogen in small quantities is not easily detected.

AMMONIA, NH_3.

33. Occurrence. — Ammonia, which is a chemical compound of nitrogen and hydrogen, is a very important substance. It occurs widely distributed in the atmosphere and in nearly all waters. Rain, snow, ice, and the waters of springs, deep and shallow wells, lakes, streams, and seas, all contain considerable quantities of ammonia.

It is a wise provision that ammonia is thus distributed, since from it plants build up the nitrogen-bearing portions of their tissues, — the albuminoids, — found in seeds, roots, and leaves. Animals, in turn, consume these tissues, and thus acquire the material for building up the nitrogen-bearing portions of their bodies, — the proteids, — found in muscles and in other parts of the body.

Ammonia compounds occur but sparingly in nature, although they are important manufactured articles of commerce.

34. Preparation and Properties. — Exp. 34. In one hand place a little powdered quicklime, CaO, and in the other put an equal bulk of powdered ammonium chloride, or sal-ammoniac, NH_4Cl. Note that neither has an odor. Rub these substances between the palms of the hands, and carefully smell the gas produced : —

$$CaO + 2 NH_4Cl = 2 NH_3 + CaCl_2 + H_2O.$$
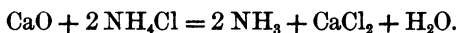
The residue in the hands is chiefly calcium chloride, $CaCl_2$.

Ex. Has ammonia a color? Place a strip of moistened red litmus paper in the fumes, and note whether they are alkaline.

In this experiment, ammonia was liberated from one of its compounds by means of a stronger, or "fixed" alkali. Since ammonia and its compounds are vaporized by the action of heat, it is called the "volatile" alkali; while all other alkalies are not readily vaporized, and are designated as the "fixed" alkalies. All the fixed alkalies will liberate ammonia from its compounds.

Exp. 35. To a solution of any ammonium salt in a test-tube add a solution of potassium hydroxide, KOH. Warm the tube gently, and test as usual the properties of the gas evolved. Test the alkalinity of the gas by means of a moist red litmus paper.

Ammonia gas dissolved in water is sold in every drug store as *aqua ammoniæ*. Aqua ammoniæ is prepared from about the same materials used in Exp. 34. The ammonium chloride or sulphate is procured from gas-works, where it is obtained as a by-product by passing the crude gas from the retorts through dilute hydrochloric or sulphuric acid.

The interesting process of manufacturing aqua ammoniæ is illustrated in Exp. 36, which also shows a general process of *dissolving gases* in water. Sometimes the gas is forced into the water by means of its own pressure, ob-

tained by closing air-tight the generator, the washing-apparatus, and the receiver.

Exp. 36.   Arrange an apparatus as in Fig. 14.   Then take (say) 50ᵍ powdered quicklime and 100ᵍ ammonium chloride, and moisten each separately with water until thick pastes are formed.   Disconnect F, and rapidly introduce these pastes into it, and join immediately with the wash-bottle A, which acts as
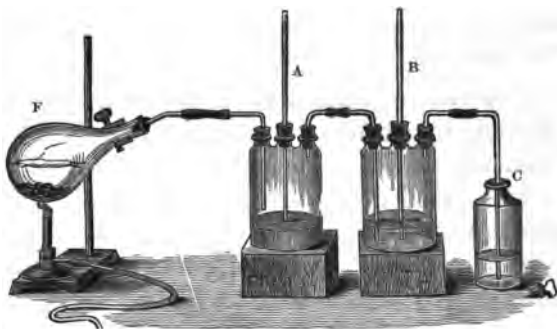
Fig. 14.

a safety apparatus to prevent any water from flowing back into the generating-flask F.   B and C are here used as condensers, and the ammonia in passing through them is dissolved in the water they contain.   It is best to surround B and C with pounded ice and salt.   Aqua ammoniæ is found in these two bottles at the conclusion of the experiment.

Ammonia is very soluble in water.   1ᶜᶜ of water, at 0° C., dissolves 1148ᶜᶜ of ammonia.

Atmospheric ammonia is produced by the decay of nitrogenous organic matter; and through the agency of atmospheric moisture it finds its way into the waters of all localities.

Ammonia was formerly prepared by distilling hoofs,

hides, and horns, whence arose the name of "spirits of hartshorn."

Exp. 37. Place a few drops of ammonia on a piece of porcelain or platinum foil, and carefully evaporate to dryness. Next treat in a similar manner a few drops of hydrochloric acid, HCl. Does either give a residue? Now make a mixture of the two, and proceed as before. Note the residue.

Ammonia unites with acids to form salts, as shown in the foregoing experiment: —

$$NH_3 + HCl = NH_4Cl.$$

The salt is called ammonium chloride, and the group of atoms, NH_4, is called *Ammonium*, owing to some resemblances which it bears to the metals.

Under a pressure of seven atmospheres, at 15.5° C., ammonia condenses to a liquid. When this liquid vaporizes, as in the case of water, large quantities of heat are rendered latent. Advantage has been taken of this to manufacture ice. Liquid ammonia is simply allowed to evaporate in closed iron pipes over which water is slowly trickling.

Since ammonia neutralizes acids, it may be applied when acids are spilled on the clothes or on the flesh. Again, when poisonous or irritating gases have been inhaled, ammonia vapors act as an antidote. When ammonia is inhaled, it produces a stimulating effect upon the system.

35. Tests for Ammonia. — To a solution supposed to contain ammonia add a solution of potassium hydroxide, KOH, and warm gently. If ammonia be present, it may be recognized —

(1) By its odor.

(2) By its turning moistened red litmus paper blue.

(3) By holding a warm glass rod, which has been mois-

tened in hydrochloric acid, over the tube, white fumes of ammonium chloride, NH$_4$Cl, may be seen, and the rod when dry will be found coated with the same salt.

NITROGEN AND OXYGEN.

36. There are five compounds of nitrogen and oxygen known : —

Nitrogen monoxide, N$_2$O.
Nitrogen dioxide, N$_2$O$_2$, or NO.
Nitrogen trioxide, N$_2$O$_3$.
Nitrogen tetroxide, N$_2$O$_4$, or NO$_2$.
Nitrogen pentoxide, N$_2$O$_5$.

Of these compounds, the first is of most practical importance. All are gases except the last, which is a crystalline solid. The last four will receive but a passing notice.

The second oxide is formed when a metal and nitric acid, HNO$_3$, react. When the gas thus produced escapes into the air, it absorbs oxygen, producing varying amounts of the next two higher oxides, and thus giving rise to the brownish red fumes always noticed when nitric acid is acting on metals, thus : —

Exp. 38. Place a bit of copper in an evaporating-dish, and add enough nitric acid to cover the copper. Warm the dish gently, and note the colored fumes above the dish : —

$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O.$$
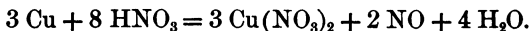
Portions of the nitrogen dioxide unite with the oxygen of the air thus : —

$$NO + O = NO_2 \ \text{and} \ 2\,NO + O = N_2O_3.$$
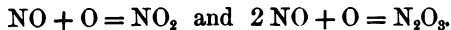
The blue salt formed is copper nitrate, Cu(NO$_3$)$_2$.

NITROGEN MONOXIDE, N₂O.

37. Preparation and Properties. — This gas is known as nitrous oxide, and also as "laughing-gas." It never occurs free, but it is manufactured by dentists and by others for anæsthetic purposes. There are several methods of obtaining nitrogen monoxide, but the one always used consists in decomposing ammonium nitrate, NH_4NO_3, by means of heat : —

$$NH_4NO_3 \text{ (heated)} = N_2O + 2 H_2O.$$

EXP. 39. Place in a test-tube a small quantity of ammonium nitrate, and heat it carefully in the Bunsen flame. Note the odor of the gas produced, and test it with a glowing match and then with a blazing match. Compare the results with those obtained in oxygen.

For generating large quantities of nitrous oxide, commercial ammonium nitrate is often employed. Coming from this source, the gas is apt to contain impurities dangerous to inhale, such as nitrogen dioxide, NO, and perhaps some chlorine or chlorine compounds. In order to remove these impurities, the gas is washed, as shown in the following experiment, which also illustrates the usual method of *washing gases* : —

EXP. 40. Arrange an apparatus as shown in Fig. 15. The generator is fitted with a bent, one-bulb, thistle-top tube, containing a small quantity of mercury. This makes a safety-valve. The first wash-bottle contains a warm solution of ferrous sulphate, $FeSO_4$, to remove any nitrogen dioxide. The second bottle contains a warm solution of potassium hydroxide, KOH, to remove any chlorine. The third bottle contains warm water. Use about 50^g of ammonium nitrate in the generator, and employ a moderate heat. Collect the gas in gas-bags, as it is soluble in water, and more especially in cold than

in warm water. Inhale some of the gas thus prepared, and note the odor and the sweetish taste.

When inhaled in considerable quantities, nitrogen monoxide produces its effects upon the system in the following order: intoxication, and singing in the ears; insensibility; and finally, if the inhalation be continued long enough, death.

FeSO₄   KOH   H₂O
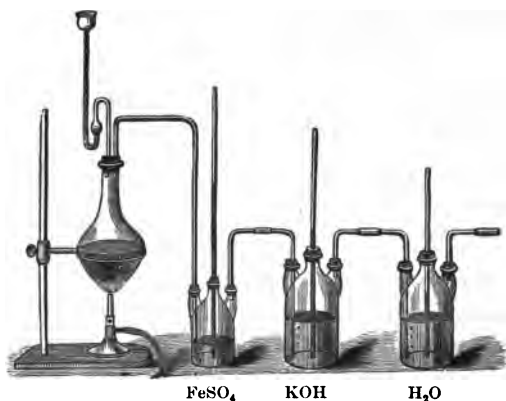
FIG. 15.

At 0° C., 30 atmospheres' pressure condenses this gas to a liquid; and if this liquid be mixed with carbon bisulphide, CS_2, and evaporated *in vacuo*, the very low temperature of −140° C. is produced.

38. Tests for Nitrogen Monoxide. — This gas closely resembles oxygen, from which it is easily distinguished by its sweetish taste and odor, and by its solubility in cold water.

39. The Law of Multiple Proportions. — By inspecting the formulæ of the oxides of nitrogen, it will be seen that the

quantities of oxygen that are united with N, are to one another as $1:2:3:4:5$, while the nitrogen remains constant.

Such relations as these are frequently found in the compounds of elements. In every case the ratio is a simple one, and the element that increases does so by whole numbers, and not by fractions. This is in strict conformity with the atomic theory. The law of multiple proportions may be stated thus : —

If two elements, A and B, form several compounds with each other, and if we take any fixed amount of A, then the different quantities of B which combine with this fixed amount of A bear a simple ratio to one another.

40. Determination of Molecular Weights. — The molecule of any substance has been defined as the smallest particle of that substance which can exist in a free state. If now we take a molecule of a gas like hydrochloric acid, HCl, that molecule must have at least one atom each of hydrogen and chlorine, and its molecular weight will be the sum of the weights of these two atoms. Thus, for hydrochloric acid we have $1 + 35.5 = 36.5$. Therefore in such simple gases, where the atomic weights are known, the problem presents no difficulties. But when the constitution of a gas is more complex, as in the second and fourth oxides of nitrogen, difficulties arise. But it has been found that when the molecular weight of a gas is divided by its specific gravity, a nearly constant quantity is obtained, *i.e.* about 28.88. Hence it follows that in any gas the molecular weight = the *specific gravity* × 28.88. In such cases, then, the specific gravity of the gas gives a key to the molecular weight. Thus, in the second

oxide of nitrogen, the specific gravity found is 1.03845. Now $1.03845 \times 28.88 = 29.99$, or practically 30. This would make the molecular formula NO, and not N_2O_2. In the same way the molecular weight of the fourth oxide of nitrogen was found to be about 46, and its formula NO_2. There is no certain method of determining the molecular weights of substances which cannot be vaporized.

41. Avogadro's Hypothesis. — Avogadro explained the relation existing between the molecular weight and the specific gravity of a gas by the following hypothesis : *Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules.* Thus if one cubic centimetre of one gas has (say) 1000 molecules, then a cubic centimetre of any other gas under the same conditions will also have 1000 molecules. This hypothesis has been of the greatest importance to a correct conception of some facts in theoretical chemistry. See

THE COMPOUNDS OF NITROGEN, OXYGEN, AND HYDROGEN ; OR, THE NITROGEN OXACIDS.

42. These three elements unite to form three compounds, called acids : —

Hyponitrous acid (hypothetical),	HNO.
Nitrous acid,	HNO_2.
Nitric acid,	HNO_3.

Only the last two acids have been isolated, and none of them occur free in nature in any considerable quantity. Nitric acid is the most important acid of this series,

Nitrous acid may be prepared by dissolving nitrogen trioxide in water : —

$$N_2O_3 + H_2O = 2\,HNO_2.$$
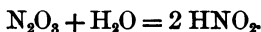
This acid is unimportant, but its salts — the nitrites — occur in impure well-water, being produced during the decay and nitrification of organic nitrogenous substances.

NITRIC ACID, HNO₃.

43. Occurrence. — The compounds of nitric acid, potassium nitrate, KNO_3, and sodium nitrate, $NaNO_3$, occur quite plentifully in nature, and it is from these substances that this very important acid is obtained.

44. Preparation and Properties. — EXP. 41. Place a small quantity of powdered potassium nitrate, KNO_3, in a test-tube, and then add a few drops of sulphuric acid. Warm the contents of the tube gently, and note the fumes given off. Test the fumes with moist blue litmus paper.

In this experiment, nitric acid was liberated from one of its compounds thus : —

$$KNO_3 + H_2SO_4 = HKSO_4 + HNO_3.$$
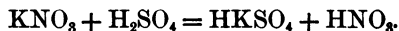
Commercial nitric acid, enormous quantities of which are consumed annually, is obtained by treating Chili saltpetre, $NaNO_3$, with sulphuric acid in large iron retorts. The vapors of nitric acid are condensed in earthenware condensers. This process may be illustrated in the laboratory by means of the apparatus shown in Fig. 16. One method of *condensation* is also illustrated by the experiment.

EXP. 42. Place in the retort A (Fig. 16) equal parts, by weight, of potassium nitrate, KNO_3, and sulphuric acid. Sur-

round the receiver R with snow or ice, or allow a stream of cold water to flow over it.   Heat the retort gently, when fumes of nitric acid will be given off and condensed in the receiver R.

Exp. 43.   Heat to redness some powdered charcoal in an iron spoon, and then cautiously add a few drops of the nitric acid, prepared as above.   Also treat a fresh portion of charcoal with powdered potassium nitrate, KNO_3.

Nitric acid and its compounds contain much oxygen, which is quite readily given up to other substances under the influence of heat.   Hence both the acid and its compounds are called *oxidizing* agents.
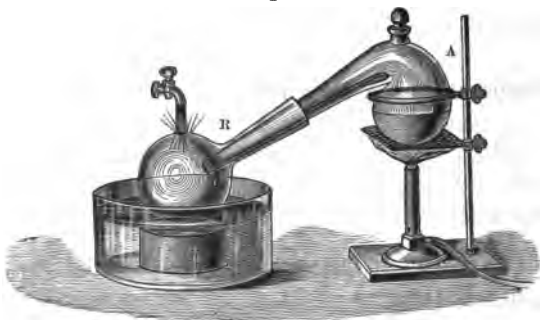
Fig. 16.

Substances containing carbon and other inflammable constituents are capable of burning in the absence of air when mixed with potassium nitrate.   Hence this compound is extensively used in the manufacture of gunpowder, which is simply a mechanical mixture of sulphur, charcoal, and saltpetre.   Again, gun-cotton is made by treating cellulose, or pure vegetable fibre, with a mixture of sulphuric and nitric acids.   Nitro-glycerine is made by treating glycerine with the same acids.

An efficient explosive owes its power to the large volume of gas that is suddenly liberated during its combustion.

Nitric acid unites with most metals to form a class of compounds called nitrates. Now these nitrates are all soluble in water; hence nitric acid is largely used in the laboratory as a solvent. In the arts this acid also finds many important uses.

45. Test for Nitric Acid. — Make a mixture of the substance to be tested with a solution of ferrous sulphate, $FeSO_4$, in a test-tube. Now carefully add a small quantity of sulphuric acid, without mixing with the contents of the tube. The sulphuric acid will sink to the bottom of the tube, and where the two liquids meet a brown ring will appear. Sometimes the formation of the ring will be aided by tapping the test-tube lightly with the finger. If the contents of the tube be now mixed, the ring will disappear and the solution become colorless.

NOTE. Bromides and iodides will give nearly this same test, but the solution will not lose so much of its color when shaken when either of these substances is present. But it is always best to test for these substances, when working an unknown, before reporting nitric acid.

EXERCISES.

(For Review or Advanced Course.)

1. How many grammes of laughing-gas may be had from 100^g NH_4NO_3? If one litre of this gas at $0°$ C. and 760^{mm} pressure weighs 1.972^g, how many litres of this gas will be obtained?

2. By adding one molecule of water to the first, third, and fifth oxides of nitrogen, the following results will be obtained: —

$N_2O + H_2O = 2\,HNO$; $N_2O_3 + H_2O = 2\,HNO_2$; $N_2O_3 + H_2O = 2\,HNO_3$.
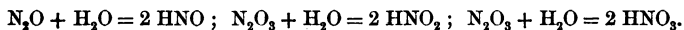
What acids are thus produced? Can the first one be actually produced in that way? Oxides which behave thus are called *Anhydrides.* Define anhydrides.

3. The specific gravities of three of the nitrogen oxides are respectively 1.527 ; 1.038 ; 1.5909. What are the corresponding molecular weights of these oxides, and what their molecular formulæ ?

4. The specific gravities hitherto given refer to air as the standard, or air $= 1$. Sometimes hydrogen is used as the standard. Now it is evident that the hydrogen molecule, H_2, weighs twice as much as the hydrogen atom. Knowing the atomic weights, it is easy to find the density (which is numerically equal to the specific gravity) of gases when referred to the hydrogen unit. Thus, in ammonia, NH_3, the molecular weight is $14 + 3 = 17$. Now, according to Avogadro's hypothesis, equal volumes of hydrogen and of ammonia under like conditions contain the same number of molecules. Whence it follows that if hydrogen be taken as 1, the density of ammonia is $17 \div 2 = 8.5$. A like manner of reasoning will show that the density of any gas referred to the hydrogen unit may be found *by dividing the molecular weight by 2.* Determine the densities of N_2O ; N_2O_3 ; N_2O_4.

5. Read Remsen's Theoretical Chemistry, pp. 32–38, for a fuller discussion of Avogadro's hypothesis and the determination of the molecular weights of the elements and of compounds. Also see Meyer's Modern Theories of Chemistry, pp. 7–17.

6. Write a sketch of the chemist Rutherford, who discovered nitrogen in 1772.

7. How many grammes of ammonia can be obtained from 100ᵍ of NH_4Cl ?

8. Read the experiment wherein you prepared nitrogen. Now, why can you not prepare oxygen from the air by using some substance to combine with the nitrogen ?

9. Measure the laboratory, and calculate its cubic contents. Now, if one litre of air, under standard conditions, weighs 1.2932ᵍ, how much nitrogen does the room contain ? How many grammes of ammonia would be produced if the whole of the nitrogen were combined with hydrogen ?

10. Determine approximately the amount of nitrogen in a given volume of air thus : Make a small wooden saucer-shaped boat, and on it place a small pile of fine iron filings which has been moistened with a solution of ammonium chloride. Now float the boat on some water in a convenient vessel, and place down over the whole a tall graduated glass jar. Support the jar so that it may be left standing for a few days. When the water ceases rising in the jar, measure the volume of the residual gas, and make the proper computations. The iron unites with the oxygen, and thus forms a solid. Test the residual gas for nitrogen by means of a burning match.

CHAPTER IV.

CHLORINE, BROMINE, IODINE, AND FLUORINE, AND THEIR COMPOUNDS WITH HYDROGEN AND OXYGEN.

DATA FOR COMPUTATIONS. — CHLORINE: Symbol, Cl; Molecular Formula, Cl_2; Atomic Weight, 35.5; Weight of 1^l at 0° C. and 760^{mm}, 3.173^g. — BROMINE: Symbol, Br; Molecular Formula, Br_2; Atomic Weight, 80; Specific Gravity (Water = 1), 3.1872. — IODINE: Symbol, I; Molecular Formula, I_2; Atomic Weight, 127; Specific Gravity (Water = 1), 4.948. — FLUORINE: Symbol, F; Atomic Weight, 19.

CHLORINE.

46. Occurrence. — Chlorine never occurs free in nature, owing to its intense chemism for other elements. Its compounds, however, are plentiful, and occur in large quantities. The most important compound of chlorine is sodium chloride, or common salt, NaCl. The chlorides of potassium, calcium, and magnesium also occur native, but in much smaller quantities than the sodium compound.

47. Preparation and Properties. — EXP. 44. Place a mixture of sodium chloride, NaCl, and manganese dioxide, MnO_2, in a test-tube, and add a few drops of sulphuric acid. Note the gas which is liberated, and hold in it a strip of moist blue litmus paper. After the color of the paper has disappeared, moisten the strip in ammonia, and note that the color cannot be restored. In fact, the paper is *bleached*. Also try to bleach a strip of moist unbleached cotton cloth.

EX. Try to obtain chlorine from hydrochloric acid by acting upon it with manganese dioxide, MnO_2. Describe the experiment in detail.

43

Chlorine is a heavy, greenish yellow gas, possessing remarkably active chemical properties. It was discovered in 1774 by Scheele. It is extensively used for bleaching purposes and in the manufacture of bleaching-powder (Art. 53). It seems that chlorine in the presence of moisture is capable of effecting the following chemical reaction : —

$$2\,Cl + H_2O = 2\,HCl + O.$$
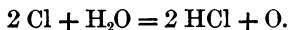
Now the oxygen thus liberated, while in a nascent state or at the instant of its liberation, possesses a stronger chemism than when in its ordinary molecular condition; thus it is enabled to combine with the coloring-matter and destroy it. It may be well to note in this connection that all elements when in a nascent state possess far more active properties than when in their ordinary conditions.

Chlorine water finds many useful applications in the laboratory. The best method of preparing a solution of chlorine in water is illustrated by the following experiment: —
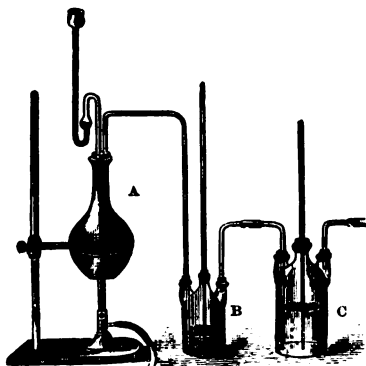
Fig. 17.

Exp. 45. In the generating-flask A (Fig. 17) place equal weights of common salt and manganese dioxide which have been pulverized and mixed. To this mixture add twice its weight of dilute sulphuric acid, consisting of equal weights of water and acid. Now apply a gentle heat, when chlorine gas will be given off abundantly. The wash-bottles B and C, which contain simply cold water, will secure the desired solution.

By disconnecting the wash-bottles, and joining instead a long glass tube, the gas may be delivered at the bottom of a tall glass jar, and thus collected by what is termed "Displacement."

The reaction which takes place in this experiment is as follows : —

$$2\,NaCl + MnO_2 + 3\,H_2SO_4 = 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + 2\,Cl.$$
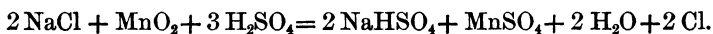
This equation is a typical one, since bromine and iodine may be prepared in the same way by substituting a bromide or an iodide for the chloride.

In testing for bromine or iodine, chlorine water is used to liberate these elements from their compounds. Chlorine water, as prepared in Exp. 45, will answer for this purpose, but a solution of chlorine may be made more quickly and more conveniently thus : —

Exp. 46. In a test-tube place a few crystals of potassium chlorate, $KClO_3$, and add sufficient hydrochloric acid to cover the crystals half an inch deep. Now warm the contents of the tube until chlorine is escaping freely, when the tube is to be filled nearly full of cold distilled water. The gas is dissolved by the water. The reaction is : —

$$4\,HCl + 2\,KClO_3 = 2\,KCl + 2\,H_2O + Cl_2O_4 + 2\,Cl.$$

The compounds KCl and Cl_2O_4 are dissolved in the water, as well as the chlorine gas, but they do not impair the efficiency of the solution.

Ex. In how many different ways have you prepared chlorine ? Try the effect of an acid upon bleaching-powder. The goods to be bleached are drawn through a tank of weak acid after they have been passed through a solution of the bleaching-powder. Why ?

48. Test for Chlorine. — Free chlorine gas may be recognized by its odor, color, and its bleaching effects upon organic colors.

CHLORINE AND HYDROGEN; OR, HYDROCHLORIC ACID, HCl.

49. Occurrence. — Hydrochloric acid occurs in small quantities in volcanic gases. But its compounds, the chlorides, as previously noticed, occur in great quantities.

50. Preparation and Properties. — Exp. 47. Place a small quantity of sodium chloride, NaCl, in a test-tube, and then add a few drops of sulphuric acid. Note the fumes that are given off when the contents of the tube are gently warmed. The reaction is : —

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

Test the fumes of this acid with a moist blue litmus paper. Will ammonia restore the color? Is hydrochloric acid a bleaching reagent?

Hydrochloric acid is an important article of commerce, and it is prepared as a by-product from the same chemicals used in the preceding experiment while treating salt with sulphuric acid in the manufacture of soda ash.

Exp. 48. Take three test-tubes, and into the first put a solution of silver nitrate, $AgNO_3$; into the second, a solution of mercurous nitrate, $Hg_2(NO_3)_2$; and into the third, a solution of lead acetate, $Pb(C_2H_3O_2)_2$. Now to each of these tubes add a few drops of hydrochloric acid. Note the heavy white precipitates which are thrown down in each tube.

Hydrochloric acid is used extensively in the laboratory for analytical purposes, as exemplified in the preceding experiment. The lead, silver, and mercury unite with the chlorine of the hydrochloric acid to form the insoluble chlorides of these metals. Now, since these three metals are the only ones that thus form insoluble chlorides, they

may be considered as forming a group which may be removed from a solution containing any or all the other metals. From this use of hydrochloric acid it is often spoken of as a *group reagent*. Again, since most of the compounds formed by hydrochloric acid are soluble in water, this acid is extensively used as a solvent.

When three volumes of hydrochloric acid are mixed with one volume of nitric acid, *Aqua Regia, or Nitro-Hydrochloric Acid*, the most powerful solvent known, is formed. This compound owes its efficiency to the fact that it furnishes large quantities of nascent chlorine to act upon the substance to be dissolved. Only a gentle heat should be employed while using this solvent, otherwise the chlorine will be driven off to waste.

It has appeared in the last experiment that hydrochloric acid is a gas. But this gas is soluble in water, one volume of water dissolving 505 volumes of the gas. The acid employed for various purposes is a solution of the gas in water. Sometimes this acid is called by one of its old names, "Muriatic Acid."

51. Test for Hydrochloric Acid. — Hydrochloric acid, either free or in any of its combinations, may be detected by adding to the solution to be tested a few drops of silver nitrate, $AgNO_3$. If hydrochloric acid be present, a white precipitate is formed, which is to be divided into two parts. To one part add nitric acid: the precipitate does not dissolve. To the second part add ammonia, and the precipitate will dissolve readily.

NOTE. Since the precipitates formed with silver nitrate by the bromides and iodides are liable to be mistaken for that of hydrochloric acid, the student must never report hydrochloric acid from this test without first testing for bromides (Art. 59) and iodides (Art. 64).

CHLORINE AND OXYGEN.

52. Chlorine and oxygen unite to form three compounds, viz. : —

Chlorine monoxide . . . . . Cl_2O.
Chlorine trioxide . . . . . Cl_2O_3.
Chlorine tetroxide . . . . . Cl_2O_4.

These compounds never occur in nature, and have not been prepared by the direct union of chlorine and oxygen. They are unimportant, and dangerous to prepare, owing to their liability to explode.

CHLORINE, OXYGEN, AND HYDROGEN ; OR, THE CHLORINE OXACIDS.

53. There are four acids in this series, but none of them are of importance in the arts or in commerce. But they serve well to illustrate some principles in chemical nomenclature, as will appear in the next chapter. The names and formulæ of these acids follow : —

Hypochlorous acid . . . . . $HClO$.
Chlorous acid . . . . . . $HClO_2$.
Chloric acid . . . . $HClO_3$.
Perchloric acid . . . . . . $HClO_4$.

The salts of some of these acids are of importance. Thus, hypochlorous acid unites with calcium to form bleaching-powder. In reality, this useful compound is manufactured by passing chlorine gas into large chambers containing slaked lime, when the following reaction is supposed to take place : —

$$2\,Ca(OH)_2 + 4\,Cl = 2\,H_2O + (CaCl_2 + Ca(ClO)_2).$$

If this be the correct explanation, bleaching-powder is a mixture of calcium chloride and calcium hypochlorite.

Chloric acid forms a class of compounds that are somewhat important, — the chlorates. Potassium chlorate, the most useful of these compounds, is prepared by passing chlorine gas into a warm concentrated solution of potassium hydroxide, thus : —

$$6\,Cl + 6\,KOH = 5\,KCl + 3\,H_2O + KClO_3.$$

The chlorates are liable to explode when brought in contact with any combustible substance, owing to the ease with which they give up oxygen. It is not safe even to grind a chlorate in a mortar with a combustible substance. When such mixtures are to be made, as when making colored fires, the materials must be ground separately, and carefully mixed afterwards on a sheet of paper. Some idea of the behavior of the chlorates may be obtained by the following experiment, which is safe if carefully conducted : —

EXP. 49. Place two small crystals of potassium chlorate in a dry iron mortar. Add a few grains of dry sugar. Now wrap a towel about the hand, and grasp the pestle in the towel. Rub the material in the mortar lightly until a good mixture is made, and then strike the pestle sharply down upon the mixed substances. A sharp explosion will ensue. If sulphur, gum shellac, or any combustible substance be used in place of the sugar, an explosion will occur.

54. Test for Chloric Acid or the Chlorates. — A chlorate, when treated with hydrochloric acid in a test-tube, will yield free chlorine gas (Exp. 46). Further, if a few crystals of a chlorate be placed in a test-tube, and sulphuric acid be added, a sharp explosion will follow.

NOTE. In making this test, a bit of cloth should be put around the tube, and the cloth is to be taken firmly in a pair of pincers. Thus the tube may be held firmly, and its mouth must not be pointed towards any apparatus or in the direction of any person in the room.

BROMINE.

55. Occurrence. — Bromine never occurs free in nature. It is chiefly obtained from the mother liquor remaining after removing the crystals of common salt in salt factories. Balard discovered bromine in the year 1826, in sea-water. Bromine is an article of commerce, but it is by no means a plentiful element.

56. Preparation and Properties. — Exp. 50. Place a mixture of potassium bromide, KBr, and manganese dioxide, MnO_2, in a test-tube, and add a few drops of sulphuric acid. Note the heavy dark-colored fumes given off.

Ex. Using the equation under Exp. 45 as a model, and substituting KBr for NaCl, write out the reaction which occurs in this experiment. For the method of preparing bromine water and liquid bromine, see Shepard's Elements, p. 109.

Bromine is a dark-colored liquid at ordinary temperatures, which always gives off pungent, irritating fumes. It is used to some extent as a disinfectant, but it is not so energetic in its action in this respect as chlorine.

Bromine of commerce is prepared by the action of chlorine on its compounds. The chlorine is generated in the mother liquor by means of the chemicals employed in Exp. 44.

57. Test for Free Bromine. — Free bromine, even in dilute solutions, when shaken in a test-tube with carbon disulphide, CS_2, colors the disulphide brownish red.

BROMINE, HYDROGEN, AND OXYGEN.

58. The compounds of bromine with oxygen and hydrogen closely resemble those of chlorine. Thus we have —

Hydrobromic acid . . . . . HBr.
Hypobromous acid . . . . HBrO.
Bromic acid . . . . $HBrO_3$.
Perbromic acid . . . . . $HBrO_4$.

None of the oxides of bromine have been prepared. None of these compounds, except hydrobromic acid, are of importance; and of the compounds formed by them, the bromides corresponding to the acid, HBr, are the only ones much used in the arts. Thus, potassium bromide, KBr, is used in medicine; silver bromide, AgBr, is used in photography; while magnesium bromide, $MgBr_2$, occurs in some mineral waters. Hydrobromic acid itself is used to some extent in organic analysis.

59. Test for Hydrobromic Acid or the Bromides. — Place the solution to be tested in a test-tube, and add a small quantity of chlorine water, to liberate the bromine. Now add a few drops of carbon disulphide, CS_2, and shake the contents of the tube thoroughly. If the substance tested be hydrobromic acid or any of its compounds, the carbon disulphide will be colored brownish red by the free bromine liberated by means of the chlorine water.

IODINE.

60. Occurrence. — Iodine never occurs free in nature. It is mostly obtained from sea-water, from which it is taken up by sea-weeds. These weeds are gathered along the

coasts of some countries, especially Ireland and Scotland, where they have been washed up by storms. The weeds are then dried, and burned in shallow trenches at a low temperature, so that the iodides of sodium, potassium, etc., may not be volatilized. Now these iodides are soluble in water, so they are removed from the "kelp," as the ashes of the plants are popularly called, by solution in water.

Plantations of these weeds are cultivated in some parts of the ocean, and at proper times vessels are sent out to gather the weeds.

Again, a considerable portion of the iodine that now comes to market is obtained from sodium iodide, NaI, found occurring along with Chili saltpetre.

61. Preparation and Properties. — Exp. 51. Place a mixture of potassium iodide, KI, and manganese dioxide, MnO_2, in a test-tube, and add a small quantity of sulphuric acid. Note the vapors evolved.

Ex. Compare this method of preparing iodine with the processes used in obtaining chlorine and bromine, and write the reaction.

Commercial iodine is prepared by the method given in the preceding experiment. The materials are placed in iron retorts, and the vapors of iodine are condensed in black, shining crystals upon the sides of suitable condensers.

Iodine is much used in medicine, especially in reducing swellings and in checking the spread of eruptive diseases like erysipelas. When thus applied, it is brought into solution by dissolving 20 parts of iodine with 30 parts of potassium iodide in 900 parts of water.

62. Test for Free Iodine. — Free iodine colors carbon disulphide, CS_2, violet.

IODINE AND ITS COMPOUNDS WITH HYDROGEN AND OXYGEN.

63. The compounds formed by iodine resemble very closely those formed by chlorine and bromine. This will appear by inspecting the formulæ of the following compounds : —

Hydriodic acid . . . . HI.
Iodine pentoxide . . . . . . I_2O_5.
Iodic acid . . . . HIO_3.
Periodic acid . . . . HIO_4.

None of these compounds are used excepting hydriodic acid, which has a limited application in analytical work. None of the compounds formed by these substances and the metals are of importance excepting potassium iodide, KI. This is much used in medicine as a sedative.

64. Test for Hydriodic Acid or an Iodide. — Add chlorine water to the substance, in order to liberate iodine. Now add to the solution a few drops of carbon disulphide, and shake the contents of the tube thoroughly. If this acid or one of its compounds be present, the disulphide is colored violet.

NOTE. The iodides give a precipitate with silver nitrate, which may be mistaken for that of chlorine or bromine. See Art. 51.

FLUORINE.

65. Fluorine is a gaseous element which has but recently been prepared. It was obtained by electrolyzing perfectly dry hydrofluoric acid, HF, in platinum tubes. Its chief compound is with calcium, as found in the mineral fluorspar, CaF_2. Fluorine forms no compounds with oxygen,

and but one with hydrogen, hydrofluoric acid, HF. This acid possesses the remarkable power of combining with glass. It may be prepared by acting on fluor-spar with sulphuric acid: —
$$CaF_2 + H_2SO_4 = CaSO_4 + 2\,HF.$$

The preparation and behavior of this acid may be shown by the following experiment: —

EXP. 52. Cover both sides of a sheet of glass with a coating of beeswax. With a sharp, soft point cut through the wax some design or some written characters. Now place some powdered fluor-spar in an evaporating-dish, and then pour on enough sulphuric acid to cover the fluor-spar. Support the glass a short distance above the dish, and warm the contents of the dish gently. Keep the whole apparatus where the fumes will not escape in the room, and in a short time the design or writing will be etched into the glass. This is best seen when the wax is removed. The fumes of hydrofluoric acid are poisonous, and must not be inhaled.

What takes place may be shown by this equation: —

$$SiO_2 + 4\,HF = 2\,H_2O + SiF_4.$$
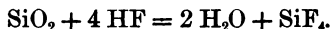
Glass is a compound of sand, SiO_2, and metals, usually sodium or potassium. The silicon tetrafluoride, SiF_4, is a gas which escapes as fast as formed: the fumes may be seen during the experiment.

The best test for fluorine is the etching test, as shown in the preceding experiment.

EXERCISES.

(For Review or Advanced Course.)

1. Make a table showing the atomic weights and physical conditions at ordinary temperatures of chlorine, bromine, and iodine. Also make a table showing the formulæ of their compounds with hydrogen and oxygen. What similarities and what differences do you find?

2. Which possesses the stronger chemism, chlorine or bromine? Chlorine or iodine? (Sug. See the tests for bromine and iodine.)

3. How many grammes of chlorine may be obtained from 100^g NaCl? How many litres would this make under standard conditions?

4. The volume of a given mass of any gas varies according to the temperature in the ratio of $273 + t : 273 + t'$, in which t is the given temperature, and t' the required temperature. Now let V be the given volume, and V' the required volume, and we have the proportion : —

$$V : V' :: 273 + t : 273 + t'.$$

By suitable transformations this proportion gives an equation suitable for solving problems concerning gases in which variations of temperature are involved : —

$$(1) \quad \frac{V}{273 + t} = \frac{V'}{273 + t'}.$$

Solve the following problem : —

PROBLEM. 5^l of chlorine gas at 15° C. become how many litres at 20° C.?

5. The volume of a given mass of gas varies inversely as the pressure or height of the barometer. Letting H be the given height of the barometer, and H' the required height, we have this proportion : —

$$V : V' :: H' : H.$$

This gives the equation —

$$(2) \quad VH = V'H',$$

an equation useful in solving problems in gases involving variations in pressure. Solve this

PROB. 10^l of oxygen gas under 760^{mm} pressure become how many litres under 758^{mm}?

6. By combining equations (1) and (2), we have : —

$$(3) \quad \frac{VH}{273 + t} = \frac{V'H'}{273 + t'}.$$

This equation is used when both temperature and pressure vary. Solve this

PROB. The barometer reads 755^{mm} and the thermometer 15° C. when 10^l of hydrogen gas were generated; how many litres will this hydrogen become when the pressure is 762^{mm} and the temperature 18° C.?

7. What per cent of KBr is bromine? Potassium? Give a rule for determining the percentage composition of any chemical compound.

8. How much silver nitrate would be required to precipitate the chlorine

in 10^g of sodium chloride?   (Sug. $AgNO_3 + NaCl = AgCl + NaNO_3$. By taking the molecular weights of these compounds, we find that 170^g of $AgNO_3$ will precipitate the chlorine in 58.5^g of NaCl.)   How much AgCl will be produced ?   How much $NaNO_3$?

9. WRITING EQUATIONS.   It is desirable to know how to write equations. · This may be understood from the following explanation : Place the formulæ of the known substances, or the substances to be experimented upon, in the first member of the equation, and connect them by the sign +.   Now determine (by experiment or otherwise) what substances are produced, and write their formulæ in the second member, and connect them also by the sign +.   If the equation now balances, it is complete. If not balanced, this rule applies : *There must be an equal number of atoms of each element in both members of the equation.*   For example, take the reaction between H_2SO_4 and KNO_3. Since these substances are known, we commence the equation thus : —

$$H_2SO_4 + KNO_3 = \cdots\cdots.$$

Experiment has shown that under certain conditions HNO_3 and K_2SO_4 are produced.   Therefore we place these formulæ in the second member, and our equation reads : —

$$H_2SO_4 + KNO_3 = K_2SO_4 + HNO_3.$$
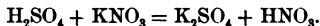
By inspection, it appears that the hydrogen atoms do not balance, so we multiply the HNO_3 by 2.   Again, the potassium atoms do not balance, so we multiply KNO_3 by 2, and the equation now balances, and reads : —

$$H_2SO_4 + 2\ KNO_3 = K_2SO_4 + 2\ HNO_3.$$
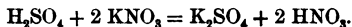
Form equations from these data : —

1. When $BaCl_2$ and K_2SO_4 react, $BaSO_4$ and KCl are produced.
2. When $Hg_2(NO_3)_2$ and HCl react, Hg_2Cl_2 and HNO_3 are produced.

CHAPTER V.

66. Binary Compounds. — We have now studied a number of chemical compounds, and it will be profitable to consider these substances from a theoretical standpoint before proceeding farther, for the purpose of arranging them in classes and of explaining some of the principles of chemical nomenclature.

We have had a number of substances like H_2O, HCl, HI, HBr, HF, etc., which consist of but two elements combined in definite proportions. Now these substances, and all others which consist of but two elements, are called *Binary Compounds*. The principal elements which form binary compounds are oxygen, sulphur, chlorine, bromine, and iodine.

It is a general rule that the names of all binary compounds shall end in "ide." Thus the binary compounds containing oxygen are called oxides, while the names sulphides, chlorides, iodides, etc., readily suggest what element enters into the compound named.

Now, since any of the "ide"-forming elements may unite with any of the metals to form an "ide" compound, it is necessary to distinguish between the compounds thus formed. This is done by prefixing the name of the metal

to that of the "ide"-forming element. Thus, KCl is called potassium chloride, NaBr is called sodium bromide, CaF_2 is called calcium fluoride, etc.

Sometimes an "ide"-forming element unites in more than one proportion with another element. In such cases the prefixes "mon," "di," "tri," "tetr," "pent," etc., signifying respectively one, two, three, four, five, etc., are prefixed to the name of the "ide"-forming element. Thus we have chlorine monoxide, Cl_2O; chlorine trioxide, Cl_2O_3; etc. The nitrogen oxides also furnish further examples.

Ex. Student name the following: CaO; I_2O_5; SiF_4; KF; HBr; CaS; LiCl; NaBr.

There are some of the metals which form two classes of compounds. In such cases the name of the metal is modified by the suffixes "ous" and "ic." Thus we have Hg_2Cl_2, mercurous chloride, and $HgCl_2$, mercuric chloride. The principal metals forming such distinct classes are mercury, iron, copper, tin, and lead. Examples of these will appear further on in their appropriate places.

When more than two classes of compounds are formed, other means of distinguishing them are employed. Thus manganese forms the oxides MnO, manganous oxide; Mn_2O_3, manganic oxide; Mn_3O_4, manganoso-manganic oxide, *i.e.* consisting of manganous and manganic oxides; and MnO_2, manganese dioxide.

Sometimes the relation of 2 to 3 is indicated by the word "sesqui"; thus, Fe_2O_3, sesqui-oxide of iron. But the most recent name for this compound is ferric oxide. It will be noticed that in the cases of iron, copper, tin, lead, and some other metals, the Latin names are used when naming the two classes of salts.

67. Higher Compounds are those containing more than two elements combined in definite proportions. Examples of these are already familiar to the student.

68. Acids. — In the preceding pages the word *acid* has been used many times, and several acids have been prepared and tested. It is difficult to give a concise definition of an acid, but in general we may say that it is a hydrogen compound usually having a sour taste and corrosive properties; it is capable of changing vegetable colors, as in turning blue litmus red; and it can give up some or all of its hydrogen and take a metal instead.

There are both binary and higher acids. The principal binary acids have already been studied. Thus we have had HCl, hydrochloric acid, or hydrogen chloride; HBr, hydrobromic acid, or hydrogen bromide; etc. We shall also see that sulphur and some other elements form with hydrogen binary acids. This class of acids is often called the hydrogen acids, or the hydracids, to distinguish them from the higher acids, which contain oxygen.

We have also had experience with a goodly number of the higher, or better, the oxygen acids. Thus, HNO_3, nitric acid; $HClO_3$, chloric acid; $HBrO_3$, bromic acid; etc. In naming these acids, it is a rule that the most common, the most important, or the one first discovered, shall have a name ending in " ic," and that this suffix shall be joined to the name of the acid-forming element, thus: —

> Nitric acid, HNO_3,
> Chloric acid, $HClO_3$,
> Sulphuric acid, H_2SO_4, etc.

The acid having one less atom of oxygen than the " ic " acid has " ous " prefixed to the name of the acid-forming

element; the acid with one less atom of oxygen than the "ous" acid is called the "hypo-ous" acid; while that with one atom of oxygen more than the "ic" acid is called the "per-ic" acid. All this will become apparent by an examination of the formulæ of the chlorine oxacids.

When more acids than those just enumerated appear in a series, other means of naming them are employed, as will become apparent in the sulphur oxacids.

69. Bases. — The word *base* is used differently by different chemists. Some define a base as being any substance that will unite with an acid, to remove part or all of the hydrogen of that acid, and to form a substance called a salt. This is a sweeping definition, and would include at least three different classes of substances, viz.: (1) the metals; (2) the metallic oxides; (3) the hydroxides, which are compounds of the metals and the radical hydroxyl, OH. As examples of the hydroxides, we may mention potassium hydroxide, KOH; sodium hydroxide, NaOH; calcium hydroxide, $Ca(OH)_2$; barium hydroxide, $Ba(OH)_2$; etc. Many chemists apply the word *base* to the hydroxides only.

70. Salts. — When an acid and a base react, the acid parts with all or a part of its hydrogen, and forms a compound called a salt. Thus, when a metal like zinc reacts with hydrochloric acid, the hydrogen of the acid is set free, and the salt, zinc chloride, is produced thus : —

$$Zn + 2\,HCl = ZnCl_2 + 2\,H.$$
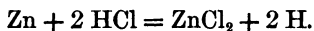
This is generally true of acids and metals, with a few exceptions. Nitric acid forms an important exception, since under ordinary conditions, while salts called nitrates are formed, no hydrogen is liberated, but, instead, water,

H$_2$O, and nitrogen dioxide, NO, are produced. The following equation is a typical one for nitric acid and a metal : —

$$3 \, Cu + 8 \, HNO_3 = 3 \, Cu(NO_3)_2 + 4 \, H_2O + 2 \, NO.$$
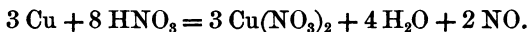
When an oxide and an acid react, a salt and water are produced, thus : —

$$BaO + H_2SO_4 = BaSO_4 + H_2O.$$
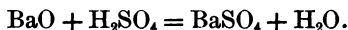
When the reaction is between a hydroxide and an acid, a salt and water are also formed : —

$$\cdot \quad KOH + HCl = KCl + H_2O.$$
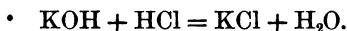
Thus it appears that a fair definition of a salt would be : A salt is an acid in which all or a part of its hydrogen has been replaced by a metal.

71. Normal, Acid, and Basic Salts. — When all of the hydrogen of an acid has been replaced by a metal, a normal salt is obtained; thus, K$_2$SO$_4$, potassium sulphate, is a normal salt. When only a part of the hydrogen has thus been replaced, an acid salt is produced; thus, HKSO$_4$, acid potassium sulphate, is an acid salt.

An oxide or a hydroxide of a metal may unite with a normal salt to form a *basic salt*. Thus : —

$$HgSO_4 + 2 \, HgO = Hg_3SO_6.$$
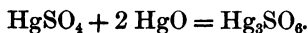
In this case basic mercuric sulphate is formed. Again : —

$$Pb(NO_3)_2 + Pb(OH)_2 = 2 \, PbOHNO_3.$$
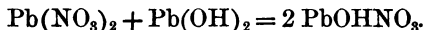
Water may also produce a basic salt thus : —

$$Bi(NO_3)_3 + 2 \, H_2O = Bi(OH)_2NO_3 + 2 \, HNO_3.$$
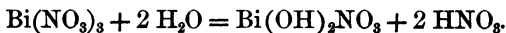
We will now explain how the salts derived from the different acids are named. In the case of the salts from the binary acids what has been said under binary com-

pounds will apply, and no further explanation is necessary. But when we come to the salts from the oxacids, further explanation is necessary.

It is a rule that when the name of the oxacid ends in " ic," the name of the salt shall end in " ate "; and when the acid ends in " ous," the salt shall end in " ite." This will be understood by examining the potassium salts of the chlorine oxacids, as follows : —

Hypochlorous acid, $HClO$, forms potassium hypochlorite, $KClO$.
Chlorous acid, $HClO_2$, forms potassium chlorite, $KClO_2$.
Chloric acid, $HClO_3$, forms potassium chlorate, $KClO_3$.
Perchloric acid, $HClO_4$, forms potassium perchlorate, $KClO_4$.

In naming the acid salts it is best to indicate the number of atoms of the metal present by the usual prefixes. Thus, sodium and phosphoric acid form two acid salts, NaH_2PO_4, monosodium phosphate, and Na_2HPO_4, disodium phosphate. The normal salt is called simply sodium phosphate, Na_3PO_4.

72. Valence. — Let us examine the following formulæ : HCl; H_2O; H_3N; H_4C. Now these actually represent compounds, and in them we see that chlorine, oxygen, nitrogen, and carbon differ in the number of hydrogen atoms that each holds in combination. This is explained by saying that each of the elements named has a different valence. In order to measure the valence of an element, we may take a simple atom like the hydrogen atom. Let this be the standard, and it follows that chlorine is univalent, oxygen is bivalent, nitrogen is trivalent, and carbon is tetravalent. If we wish to measure the valence of an element that does not unite with hydrogen, we may take some other univalent element, like chlorine, which does unite with the element in question.

It must not be inferred that valence is an unvarying property, since many elements appear to have different valences in different compounds. Thus, in HCl chlorine is univalent, while in $HClO_3$ it is pentavalent. Likewise, phosphorus in PCl_3 is trivalent, while in PCl_5 it is pentavalent. The most common valences of the elements are indicated in the table, Art. 10, by small Roman numerals or by indices written to the right and above the symbol. Usually the symbols are written without these.

73. Substituting Power and Valence. — We have already noticed how the hydrogen of an acid is replaced by a metal to form a salt. This replacement takes place according to fixed laws, depending upon the valence of the metal. Thus a univalent metal will replace one atom of hydrogen, a bivalent metal will replace two atoms of hydrogen, etc. If the acid molecule does not contain a sufficient number of hydrogen atoms to equal the valence of the metal, the acid must be multiplied by some figure to make them equal. Thus, Ca'' is bivalent; when it unites with HNO_3, the acid must be multiplied by 2 in order to satisfy the requirements of the bivalent calcium. $Ca(NO_3)_2$ is produced. Other cases arise, but they will offer no difficulty.

74. Determination of Atomic Weights by Avogadro's Hypothesis. — Elements that form compounds that are gases or may be converted into gases may have their atomic weights determined by means of Avogadro's hypothesis. First the molecular weight of each available compound of that element is ascertained. Then each compound is analyzed, and the proportions noted in which its constituents combine. Then the smallest number which occurs in any of the compounds analyzed is taken as the atomic weight.

EXERCISES.

(*For Review or Advanced Course.*)

1. If to the number which represents the valence of an element we assign a positive or negative sign, the sum of these numbers in any stable chemical compound will always equal 0, provided we let $H = +1$, $O = -2$; and the metals are to be assigned $+$ indices, except such as form binary compounds with hydrogen.

These data may be utilized to *determine the valence* of an element in any compound; *e.g.* What is the valence of Cl in $HClO_4$? Now $H = +1$ and $O_4 = -8$. What is needed to add to the $+1$ to make a number sufficiently great so that when it is added to a -8, the sum shall be 0? That number is evidently $+7$, which equals the valence of Cl in this particular compound.

Ex. Determine the valence of chlorine in all its oxacids.

2. Many chemists prefer to write what are called molecular equations. Most of those already given are what might be termed atomic equations, since they are supposed to indicate what takes place when the elements of a molecule are torn apart and thus brought into the atomic or nascent state. But atoms probably do not remain in this state, but immediately seek out other atoms with which they may unite to form new molecules. When a simple gas like hydrogen or oxygen is liberated, the hydrogen atoms unite to form hydrogen molecules; thus, $H + H = H_2$. So, likewise, with oxygen or any element. Molecular equations, then, represent what has taken place after this re-arrangement is effected. In writing molecular equations it is only necessary to have each free gaseous element appear as a molecule; thus $K + H_2O = KOH + H$ is written $2 K + 2 H_2O = 2 KOH + H_2$.

Ex. Rewrite in molecular equations all suitable atomic equations previously given. Read Meyer's Modern Theories of Chemistry, pp. 195–204.

CHAPTER VI.

CARBON AND SOME OF ITS COMPOUNDS WITH HYDROGEN, OXYGEN, AND NITROGEN.

CARBON.

DATA FOR COMPUTATIONS. — Symbol, C; Atomic Weight, 12; Specific Gravity: Diamond, 3.5 to 3.6; Graphite, 2.25; Charcoal, 1.57.

75. Occurrence. — Carbon occurs widely distributed. In the free condition it is found in transparent crystals as *Diamonds*, and in opaque, six-sided slabs as *Graphite*. In impure forms it constitutes the greater portion of *Coal*, *Soot*, and *Lampblack*. But the largest quantities of carbon are found combined with hydrogen, oxygen, nitrogen, and a few other elements, in plants, and in all living structures. Again, large quantities of carbon occur in the carbonates and in carbon dioxide.

76. Preparation and Properties. — EXP. 53. Ignite a match, and hold in the flame a bit of cold glass. What is deposited on the glass? Extinguish the match, and dip the glowing coal in water. What kinds of carbon have you thus prepared? Where is soot deposited?

Lampblack is prepared on the large scale by burning resins or oils in a limited supply of air. The lampblack is collected on suitable condensers. Charcoal is made by burning wood in a limited supply of air in coal kilns, or by distilling wood in large closed retorts. When distil-

lation is used, valuable products, such as tar and acetic acid, are obtained by condensing the vapors.

EXP. 54. Color about 50^{cc} of water with any organic color, such as cochineal or litmus solution. Place in a generating-flask some freshly burned charcoal which has been finely pulverized, or, better, some good boneblack, and then add about half of the colored solution. Shake the contents of the flask for some time, and then filter. Compare the color of the filtrate with that of the solution which was not treated. What change do you notice?
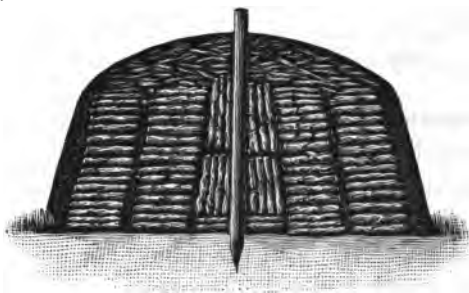
FIG. 18.

Charcoal is very porous, and it has a wonderful power of absorbing gases. Its pores therefore contain much atmospheric oxygen. Now when certain vegetable or animal substances are brought in contact with this oxygen, they are oxidized and thus destroyed. This property of charcoal is largely utilized in refining sugar, in making water-filters, and for disinfecting purposes. Charcoal made from blood is best for these uses, but sugar-refiners mostly use *Boneblack*, which is made by charring bones. Charcoal from wood is principally used in water-filters. Wood charcoal is prepared by burning wood in charcoal kilns (Fig. 18).

Ex. Why should a water-filter be cleaned and renewed frequently, and why often allowed to run dry ? How can you obtain carbon from kerosene oil ? From illuminating-gas ? What makes a lamp smoke ? For what purposes is charcoal used in the arts ?

Stone Coal is the remains of a magnificent vegetation which flourished during the carboniferous age and some of the periods following. Heat and pressure are the probable agents which converted this vegetation into stone coal. When the heat and pressure were great, *Anthracite*, or "hard" coal, was produced ; and when these agencies were less intense, *Bituminous*, or "soft" coal, was formed.

Lignite is a soft coal of more recent origin, being derived from deciduous trees similar to those now living.

Peat and *Turf* consist largely of the roots and stems of low-growing herbs such as grasses and weeds.

Ex. For what purposes are the different kinds of coal employed ? Where is peat largely used ?

Graphite, also known as "plumbago" and "black lead," has been artificially produced in insignificant quantities in iron furnaces. But it occurs native quite plentifully in many localities. It is largely used for making lead-pencils and crucibles. For these purposes it is mixed with clay. Graphite is also used for polishing purposes, in coating powder and shot, in electrotyping, and in the manufacture of stove-blacking.

Gas Carbon is found in the retorts used for distilling coal in the manufacture of illuminating-gas. This form of carbon is much employed in making plates for galvanic batteries and for making carbon pencils for electric lamps.

Diamonds are found in Africa, India, South America, and in some of the United States. They occur in earthy detritus or in clayey shales: the method of their formation is not understood.

The primary form of the diamond crystal is octahedral (Fig. 19), but it occurs also in many other forms derived from this primary form.

Diamonds vary in color from the pure, limpid variety to the black diamond, or *Carbonado*. The colorless diamond is highly prized as a jewel, while the yellowish variety is less esteemed. Blue and green diamonds are beautiful and rare, and consequently high in price.

The diamond is insoluble in acids and in alkalies; it refracts light strongly, whence arises its brilliancy; it is
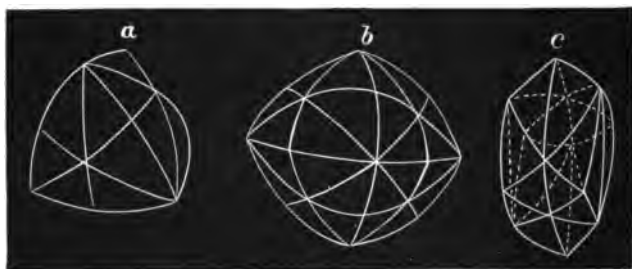
FIG. 19. — Crystals of Diamond.

the hardest substance known and does not tarnish under any circumstances, and it is to these properties that it owes its value as a jewel.

At high temperatures the diamond will burn in an atmosphere of oxygen, forming carbon dioxide, CO_2, and leaving a small amount of ash; in fact, it is almost pure carbon.

Low-grade diamonds are used for cutting glass and for writing on glass. Diamond dust is used in polishing hard and refractory substances, including the rough diamond itself. Black diamonds are extensively used for drill-points. Equipped with these drills, the miner bores

through the hardest rock with ease; and thus he is enabled to explore the earth to a depth of thousands of feet while searching for its hidden treasure.

Exp. 55.   Heat a few grains of sugar in an iron spoon or on a bit of porcelain. Do you obtain carbon? Thus try starch, beeswax, paraffin, tallow, and gum arabic. If the substance burns with a flame, hold a cold piece of metal or glass in the flame.   Are all these carbon compounds?

In this way it may be shown that all substances of vegetable and animal origin are compounds of carbon.   In short, so great is the number of these compounds that they are usually treated under a separate heading or in a book devoted exclusively to them.   This branch of Chemistry is called *The Chemistry of the Carbon Compounds*, or *Organic Chemistry*.

77. Tests for Carbon. — Free carbon is readily recognized in any of its forms by its physical properties.

CARBON AND HYDROGEN.

78. Carbon and hydrogen unite to form a multitude of compounds.   In this chapter we shall note but three of these compounds, reserving further notice to a succeeding chapter.   The names and formulæ of the three to be considered here are : —

$$
\begin{array}{ll}
\text{Methane, or marsh gas} \ldots \ldots & CH_4. \\
\text{Ethylene, or olefiant gas} \ldots & C_2H_4. \\
\text{Acetylene} \ldots \ldots \ldots & C_2H_2.
\end{array}
$$

METHANE, CH_4.

79. Preparation and Properties. — Exp. 55.   Mix 2^g sodium acetate, $NaC_2H_3O_2$, which has been thoroughly dried, with 8^g

sodium hydroxide, NaOH, and 2ᵍ finely powdered quicklime, CaO. Fit a jet delivery-tube to a hard glass test-tube; place the mixture in the test-tube, and heat the contents in the Bunsen flame. When the gas issues freely, hold moistened strips of red and blue litmus paper in it, and finally ignite it. The reaction is

$$NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4.$$

Ex. Is methane an acid? An alkali? Is it inflammable? Deliver a small quantity of the gas in a large test-tube, and mix it thoroughly with air; apply a match to the mouth of the tube. Is methane explosive?

Methane occurs in nature very plentifully, especially in connection with coal and in the oil regions. *Natural Gas*, which has lately risen to such a degree of usefulness, consists largely of methane. In coal mines it forms the miner's dreaded "fire damp," which is responsible for the numerous mine explosions that frequently occur.

Methane also occurs in marshy places and in stagnant pools, being produced by the decay of organic substances. From this fact it derived the name *Marsh Gas.*

Methane is neither an acid nor an alkali; but as we shall see further on, it is important, in that it is the lowest member of a series of hydrocarbon compounds, many of which are of the greatest utility.

Fɪɢ. 20.

Methane is not readily acted on by reagents , hence it affords no common *test* other than the color of its bluish yellow, non-luminous flame, taken together with its explosive properties.

Ex. Write a short sketch of Sir Humphry Davy, who invented the miner's safety-lamp (Fig. 20.)

ETHYLENE, OR OLEFIANT GAS, C_2H_4.

80. Ethylene is formed by the destructive distillation of coal; consequently it always forms a valuable constituent of coal gas.

Exp. 56. Place 10^g ethyl alcohol, C_2H_6O, in a generating-flask which has been provided with a jet delivery-tube; add 50^g sulphuric acid; heat gently, and note the gas which escapes. Finally ignite the jet, and note the flame, which is the same as the ordinary luminous gas-flame. The sulphuric acid simply deprives the alcohol of one molecule of water: —

$$C_2H_6O - H_2O = C_2H_4.$$

Exp. 57. Nearly fill the bowl of a common clay pipe with powdered bituminous coal, and then close the mouth of the bowl by a covering of wet clay. Now dry the clay, and heat the bowl of the pipe in the Bunsen flame, and ignite the gas escaping from the stem of the pipe. It is *Illuminating-Gas*. When the gas is all driven out, examine the contents of the bowl. *Coke* remains.

Illuminating-gas is a mixture of hydrogen, methane, ethylene, carbon monoxide, CO, and small quantities of various other gases. One of the by-products formed in distilling coal is *Coal Tar*. From this remarkable substance many useful products have been obtained, among which are many beautiful dyes.

81. Test for Ethylene. — If through a jar of ethylene chlorine gas be passed, a heavy oily liquid, ethylene chloride, $C_2H_4Cl_2$, often called "Dutch liquid," will be formed; the odor of this substance resembles that of chloroform.

Acetylene, C_2H_2.

82. Acetylene is also a gas possessing a disagreeable odor. It is formed when an ordinary Bunsen burner strikes back and burns at the base. This gas is remarkable, since it is the only compound of hydrogen and carbon that has been prepared by the direct union of these elements. The method of its synthesis is extremely simple: powerful electric sparks are passed between carbon terminals in an atmosphere of hydrogen. The odor of acetylene betrays its presence.

CARBON AND OXYGEN.

83. Two oxides of carbon are known: —

Carbon Monoxide, CO;
Carbon Dioxide, CO_2.

Of these gases, the latter is the most important. The monoxide is formed when carbon is burned in a limited supply of air: — $C + O = CO$.
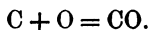
This is an inflammable, poisonous gas burning with a bluish flame, as seen in the flickering flames above the burning coal in coal stoves and grates. When carbon monoxide burns, it is oxidized to the dioxide thus: —

$$CO + O = CO_2.$$
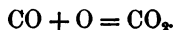
Carbon Dioxide, CO_2.

84. Occurrence. — This important gas, often called carbonic acid gas, occurs very plentifully in nature. It occurs free in the atmosphere in small but almost unvarying proportions, and it is from this source that plants obtain nearly all their supply of carbon. Limestone, $CaCO_3$,

and other mineral carbonates form a large proportion of the earth's crust.   Shells and many coral formations are almost pure limestone.

85. Preparation and Properties. — Exp. 58.   Place a small quantity of calcium hydroxide solution in a small beaker. Using a glass tube, force the breath through this solution. Note the white precipitate formed : —

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$
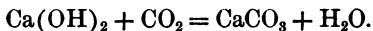
The carbon dioxide comes from the breath.   Continue to pass the breath through the solution, and the precipitate dissolves.

Carbon dioxide is one of the waste products of the body. Every air-breathing animal exhales this gas at every breath.

Exp. 59.   Place a burning taper in a wide-mouthed bottle, and cork the bottle loosely.   When the taper is extinguished, remove it, and pour into the bottle a little calcium hydroxide solution.   Shake thoroughly.   Do you obtain a white precipitate ?   Is carbon dioxide present ?   Whence came it ?   What equation applies ?

Every carbon-bearing compound when burned in the air produces carbon dioxide.   Volcanoes also send out large volumes of this gas.

Exp. 60.   Make a dilute solution of sugar, and add a little baker's yeast.   Fill a test-tube with this solution; also place a small quantity of the same in an evaporating-dish.   Invert the test-tube, and place its mouth below the solution in the dish, and allow the whole to stand in a warm place.   *Fermentation* soon sets in; bubbles of gas rise and fill the tube.   Turn this gas out into a clean test-tube, pouring the gas as if it were a liquid, and then test the contents of the second tube for carbon dioxide.

During fermentation and in the natural decomposition of all organic substances, carbon dioxide is liberated. The atmosphere contains by volume from 2.7 to 3.5 parts of carbon dioxide in 10,000.

Ex. In what ways is carbon dioxide liberated in a living-room ? In the atmosphere ? Water containing carbon dioxide in solution can dissolve limestone ; explain the disappearance of the precipitate formed in Exp. 58.

Exp. 61. Place about 10^g of coarsely pulverized limestone or marble, $CaCO_3$, in a generating-flask, fitted with a V-shaped delivery-tube. Cover the limestone with dilute hydrochloric acid, and warm gently if necessary. The following reaction occurs : —

$$CaCO_3 + 2\,HCl = CaCl_2 + H_2O + CO_2.$$

The gas may be collected by delivering it at the bottom of any deep and narrow vessel, or it may be stored in gas-bags.

Exp. 62. Fill a wide test-tube with carbon dioxide, and then lower into it a burning taper. What occurs ?

Exp. 63. Place a mouse in a jar of carbon dioxide. Note the rapidly fatal effects of the gas.

Exp. 64. Attach a common clay pipe to the nozzle of a gas-bag filled with carbon dioxide. Dip the bowl of the pipe in a soap-bubble solution, and allow the gas to escape, forming a bubble. Shake the bubble loose. Does it rise or fall ? Is carbon dioxide heavier or lighter than air ?

Exp. 65. Place the tip of the delivery-tube into the bottom of a test-tube filled with cold water. Allow the gas to bubble up through the water for some time. Test the water as follows : (1) Taste it. Is it acid ? Also test it with blue litmus paper. (2) To a portion of the water add calcium hydroxide solution. Did the water dissolve any carbon dioxide? (3) Boil the remainder of the water, and test as before. What effect does boiling have upon solutions of carbon dioxide in water ?

When large supplies of carbon dioxide are required, they are obtained by acting on some of the metallic carbonates by means of an acid. Thus soda-water fountains are charged by treating powdered marble with sulphuric acid. In baking-powders carbon dioxide is liberated by the reaction between sodium carbonate and cream of tartar, or acid potassium tartrate, $KHC_4H_4O_6$. Sometimes alum is injuriously employed instead of the cream of tartar.

Carbon dioxide is heavier than air, having a specific gravity of 1.529, while one litre weighs 1.965^g. In consequence of its high specific gravity, it collects in wells, caves, and mines; and many persons lose their lives by going down into places filled with this gas. It seems to produce its fatal effects by suffocation.

Carbon dioxide is a very stable compound, but its separation can be effected by the method shown in the following experiment: —

Exp. 66. Hold a piece of burning magnesium ribbon in a jar of carbon dioxide. Is carbon liberated?

Since we have a series of salts, the carbonates, the existence of a corresponding acid would be suggested. Thus if we regard carbon dioxide as the anhydride of that acid, we have: —
$$CO_2 + H_2O = H_2CO_3.$$
And we might suppose that the metals unite with this acid to form the carbonates. Again, a solution of carbon dioxide in water has a weak acid reaction to test paper. But notwithstanding all these facts, carbonic acid has not been prepared in a pure, concentrated state.
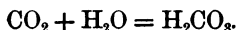
86. Tests for Carbon Dioxide and the Carbonates. — 1. If the free gas be led through a solution of calcium hydroxide, $Ca(OH)_2$, a white precipitate of calcium carbonate is formed.

2. If the free gas be in a water solution, it may be placed in a generating-flask fitted with a delivery-tube, and boiled out and passed through calcium hydroxide as before.

3. Any of the mineral carbonates will effervesce with hydrochloric acid, yielding free carbon dioxide which may be generated in a flask and tested as in 1.

CYANOGEN, CN OR Cy.

87. But one compound of carbon and nitrogen has been prepared, and that is the gas, Cyanogen. When mercuric cyanide, $Hg(CN)_2$, is heated, cyanogen is liberated; but the gas is too poisonous for the beginner to prepare.

HYDROCYANIC OR PRUSSIC ACID, HCN.

88. Prussic acid is one of the most deadly poisons known. It occurs in minute quantities. It can be prepared by treating mercuric cyanide, $Hg(CN)_2$ with hydrogen sulphide, H_2S, thus : —

$$Hg(CN)_2 + H_2S = HgS + 2 HCN.$$
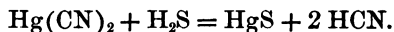
The acid has a faint and peculiar odor resembling peach blossoms. The beginner may omit its preparation.

An important class of compounds may be regarded as derived from this acid. These are the cyanides, among which is the well-known potassium cyanide, KCN, which is used in silver electroplating and as an insecticide.

89 Test for the Cyanides. — The cyanides always emit a peculiar odor resembling that of the acid. But in case of doubt a good test follows: Add to the solution potassium hydroxide, KOH, and then add ferrous sulphate, $FeSO_4$. Now shake thoroughly and acidulate the contents of the tube with hydrochloric acid. If a cyanide be present, a deep blue precipitate (Prussian blue) will be formed.

EXERCISES.

(For Review or Advanced Course.)

1. Test as many different kinds of shells as you can find for carbonates. Also test several specimens of rocks for carbonates. Usually it will be sufficient to add hydrochloric acid, HCl, and note the effervescence, without passing the gas through lime-water.

2. Read in some text on Geology a description of the carboniferous age.

3. Read all the authorities at hand on the topic of ventilation.

4. Procure a stoppered bell-jar, or a large bottle from which the bottom has been evenly cut off and ground so that it will set on a board or on the desk nearly air-tight. Let this represent a school-room. Now let a lighted taper represent the pupils sitting in the room. Make the following experiments, and show what principles they illustrate in ventilation : —

(*a*) Place the bell-jar on the desk, and insert the stopper. This now represents a room with no ventilation. Remove the stopper, insert the lighted taper, and then return the stopper. You now have a representation of a room with no ventilation, and with the pupils sitting in it. What occurs ? What lesson does this teach ?

(*b*) Most country school-houses have a hole in the ceiling for a ventilator. The jar sitting on the desk, with the stopper removed, will represent such a room. Let the air in the jar be pure, and insert the burning taper, leaving out the stopper. This arrangement represents such a room with the pupils sitting in it. What occurs, and what lesson is taught ?

(*c*) Now put the stopper in place, and let one edge of the jar project slightly over the edge of the desk. This represents a room with a ventilating opening at the bottom. Insert the burning taper when the jar is so placed. What occurs, and what is the deduction therefrom ?

(*d*) Now leave the stopper out, and let the edge of the jar project as before. We now have two openings for ventilation. Insert the lighted taper, and note the results. What is the course taken by the air ? What is the course of the circulation in the other arrangements ? What lesson have you learned ?

5. What weight of CO_2 can you obtain from 100ᵍ of $CaCO_3$? How many litres would this be under standard conditions ? At 14° C. and 758ᵐᵐ, how many litres ?

6. How could you test a well for CO_2 ? If one man loses his life in a well containing choke damp, why does another person almost invariably lose his life in the same well also ? What ought always to be done before venturing into a well ?

7. Hold a piece of fine wire gauze down over the Bunsen flame, Fig. 22. Explain what takes place.

8. Explain the action of the miner's safety-lamp, Fig. 20.

9. Generate some sulphuretted hydrogen (Art. 95), and pass the gas through a test-tube of cold water. Place the solution thus formed in a
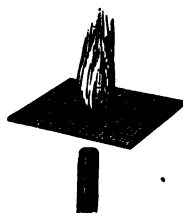
FIG. 21.   FIG. 22.

flask. Add some powdered charcoal, and shake. Has the odor disappeared? Explain.

10. What substances are produced during the combustion of hydrocarbon compounds?

11. Fill a tumbler or beaker-glass with carbon dioxide, and then pour the gas into a similar vessel containing a lighted taper (Fig. 21). Explain what occurs.

CHAPTER VII.

SULPHUR, SELENIUM, AND TELLURIUM, AND THEIR COMPOUNDS.

SULPHUR.

DATA FOR COMPUTATIONS. — Symbol, S ; Atomic Weight, 32 ; Specific Gravity (crystals), 2.05 ; Melting-Point, 115° C.; Boiling-Point, 447° C.

90. Occurrence. — Sulphur occurs native in volcanic regions. Its compounds are also widely distributed. Iron pyrites, FeS_2, or fool's gold ; galena, PbS ; cinnabar, HgS ; gypsum, $CaSO_4 + 2\ H_2O$, and heavy spar, $BaSO_4$, are among the most plentiful compounds.

91. Preparation and Properties. — Native sulphur is readily separated from its impurities by fusion. It is afterward distilled, and the vapors are conducted into suitable condensing chambers. If the chamber be cold, *flowers of sulphur* are obtained. If the temperature of the chamber is at about the melting-point of sulphur, it is obtained as a liquid which is drawn off and cast into sticks known as *roll sulphur* or *brimstone*. But the greater part of the sulphur used in the arts is simply the crude product obtained by fusion.

EXP. 67. Dissolve 1ᵍ slaked lime in 13ᶜᶜ of water. Add 2ᵍ flowers of sulphur, and boil. Now filter the solution, and acidify with hydrochloric acid. A white precipitate of finely divided sulphur is obtained. At first calcium pentasulphide,

79

CaS$_5$, is obtained; this is decomposed by the acid which is finally added. Write the equation.

The product obtained in the preceding experiment is the *lac sulphuris*, or *milk of sulphur*, of the Pharmacopœia. It is used in medicine.

Exp. 68. Place a small quantity of flowers of sulphur in a test-tube, and add carbon disulphide, CS$_2$; close the tube with the thumb, and shake till the sulphur is dissolved. Now pour the solution into a small beaker, and allow it to evaporate in the air without heat. Note the sulphur crystals obtained.

FIG. 23.

FIG. 24.

The primary form of the sulphur crystal is the octahedron (Fig. 23). But in all there are no less than thirty different forms derived from the primary crystal.

Exp. 69. Melt sulphur in a test-tube, and then heat until it becomes black and fluid. Now turn the molten mass into cold water (Fig. 24). Examine the product.

This experiment furnishes *plastic* sulphur, which strongly resembles caoutchouc. When rubber gum is heated with sulphur at moderate temperatures, a better material for some purposes is obtained than the pure gum

itself. When higher temperatures are employed, *vulcanite* or *ebonite* is obtained. Large quantities of sulphur are thus consumed.

Exp. 70. Heat a pine splinter, and dip it in flowers of sulphur. Now ignite, and note the fumes, SO_2.

Sulphur is largely employed in making matches, in bleaching straw goods and hops, in preparing sulphuric acid, and in the manufacture of gun-powder.

92. Tests for Free Sulphur. — Free sulphur can be recognized by its physical properties and by its fumes when ignited.

SULPHUR AND HYDROGEN.

93. Sulphur and hydrogen form two compounds : —

> Hydrogen sulphide, H_2S.
> Hydrogen persulphide, $H_2S_2(?)$.

Of these compounds, the first is the more important. The second has no industrial use.

HYDROGEN SULPHIDE, H_2S.

94. Occurrence. — This substance is a gas commonly called Sulphuretted Hydrogen. It occurs in large quantities, both free and combined. It is sulphuretted hydrogen that gives the offensive odor to many " sulphur springs " and mineral waters ; it is a product of volcanic action, and of the decomposition of albuminous substances, as noticed in the odor of rotten eggs. It is produced periodically in some surface wells by the action of organic substances, such as wooden curbing and wooden pumps, on iron pyrites in the presence of mineral ingredients dissolved in the waters of the wells.

95. Preparation and Properties. — Exp. 71.   Place two or three small pieces of ferrous sulphide, FeS, in a generating-flask fitted with a V-shaped delivery-tube.   Cover the lumps with water, and then add a few drops of sulphuric acid. Insert the delivery-tube, and the apparatus is now ready for use.   The reaction is : —

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$
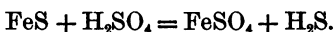
Note the odor of the gas, and finally ignite it.   Extinguish the flame, and allow the gas to bubble up through a solution of copper sulphate, $CuSO_4$, in a test-tube.   Note the precipitate formed.   Thus pass the gas through a solution of lead acetate, $Pb(C_2H_3O_2)_2$.

Hydrogen sulphide forms a series of salts, the sulphides. As in the case of hydrochloric acid, this acid is also much used in analytical work as a group reagent.   In such work, it is prepared precisely as in the preceding experiment.

96. Tests for Hydrogen Sulphide, Free or Combined. — 1. The free gas may be detected by its odor and by its blackening a strip of paper moistened with lead acetate, $Pb(C_2H_3O_2)_2$.

2. A sulphide is tested thus : Pulverize the substance to be tested, mix it with sodium carbonate, Na_2CO_3, on a bit of porcelain or platinum foil, and fuse it in the Bunsen flame.   Place the fused mass on a clean silver coin and add a drop of water.   If a sulphide be present, a black spot will appear on the silver.
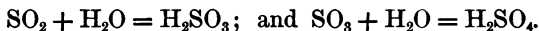
SULPHUR AND OXYGEN.

97.   We shall notice two oxides of sulphur : —

Sulphur dioxide, SO_2.
Sulphur trioxide, SO_3.

Both these oxides are important from a chemical point of view, since they are respectively the anhydrides of sulphurous acid, H_2SO_3, and sulphuric acid, H_2SO_4. They unite with water thus : —

$$SO_2 + H_2O = H_2SO_3; \quad \text{and} \quad SO_3 + H_2O = H_2SO_4.$$

The trioxide is prepared by passing a mixed stream of sulphur dioxide and oxygen over finely divided platinum in a highly heated porcelain tube. The dioxide deserves a more extended notice.

SULPHUR DIOXIDE, SO_2.

98. Preparation and Properties. — EXP. 72. Place a small quantity of powdered galena, PbS, in a hard glass tube open at both ends, and heat strongly in the Bunsen flame. Note the gas escaping from the tube.

EXP. 73. Place some fine copper filings in a test-tube, and cover with strong sulphuric acid. Heat gently, and note the escaping gas. Hold a piece of moist wheat straw in the vapors. Also try the effect upon bits of unbleached silk or woollen yarn. What occurs ? The copper and acid react thus : —

$$Cu + 2\,H_2SO_4 = CuSO_4 + 2\,H_2O + SO_2.$$

Sulphur dioxide occurs free in volcanic gases. It finds many useful applications in the arts, and is manufactured in enormous quantities. For bleaching purposes it is prepared by burning sulphur in the air. In sulphuric acid manufacture it is prepared in the same way, and also by roasting iron pyrites or some other sulphide. Of late this gas is used in manufacturing paper from wood by the sulphite process. For this purpose, the gas is run into tanks of lime-water or calcium hydroxide solution. The liquor thus prepared is used for reducing the chipped wood to paper pulp.

99. Test for Sulphur Dioxide. — Free sulphur dioxide may be recognized by its odor, which is well known, resembling that of burning matches.

THE SULPHUR OXACIDS.

100. There are eight acids in this series, as shown in the following list : —

Hyposulphurous acid	H_2SO_2.
Sulphurous acid	H_2SO_3.
Sulphuric acid	H_2SO_4.
Thiosulphuric acid.	$H_2S_2O_3$.
Dithionic acid	$H_2S_2O_6$.
Trithionic acid	$H_2S_3O_6$.
Tetrathionic acid	$H_2S_4O_6$.
Pentathionic acid	$H_2S_5O_6$.

Of these acids, but three are of importance to the beginner, — sulphurous, sulphuric, and thiosulphuric acids. The last has not been prepared, but its salts are used for some purposes, as in photography. Only the test for this acid will be given.

By inspection it will be seen that in this series of acids each contains two atoms of hydrogen. One or both of these atoms is replaceable by a metal; thus each of these acids may give rise to acid or normal salts. For example, we have acid or monosodium sulphate, $NaHSO_4$, or sodium sulphate, Na_2SO_4.

When an acid has one replaceable hydrogen atom, it is called a *monobasic* acid; when it has two, it is called *dibasic;* three, *tribasic;* and with four, it is *tetrabasic.* We have had examples of the first two; and illustrations of the others will appear further on.

SULPHUROUS ACID, H_2SO_3.

101. Preparation and Properties. — EXP. 74. Pass sulphur dioxide gas (Exp. 73) into a test-tube of cold water. Free sulphurous acid will be obtained. Write the equation.

EXP. 75. Pass sulphur dioxide gas into a solution of potassium hydroxide, KOH. Potassium sulphite will be formed: —

$$2\,KOH + SO_2 = K_2SO_3 + H_2O.$$
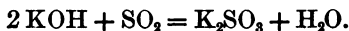
Save the acid and the salt for the tests in the next article.

Both the free acid and its salts are used to a limited extent in commerce. They both act as bleaching reagents. On standing, they absorb oxygen, passing into sulphuric compounds. When the sulphites are treated with acids, sulphur dioxide is liberated, thus: —

$$K_2SO_3 + 2\,HCl = 2\,KCl + H_2O + SO_2.$$
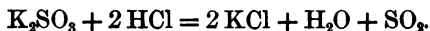
102. Tests for Sulphurous Acid and the Sulphites. — 1. Free sulphurous acid may be detected by its odor of burning matches.

2. A sulphite is detected by adding hydrochloric acid to its solution. The solution remains clear and gives off the odor of the free acid.

3. A sulphite in solution yields a white precipitate, $BaSO_3$, with barium chloride, $BaCl_2$. This precipitate is soluble in hydrochloric acid. If a portion of the barium precipitate is treated with nitric acid, the insoluble barium sulphate, $BaSO_4$, is obtained.

SULPHURIC ACID, H_2SO_4.

103. Occurrence. — Small quantities of free sulphuric acid occur in some volcanic waters. Its compounds, the sul-

phates, occur plentifully in nature.   Thus gypsum or land plaster, $CaSO_4 + 2 H_2O$, occurs in vast deposits.

It is safe to say that this is the most important acid known to chemistry and to commerce.   Although the student has this acid on his table and has used it from the very beginning of his work, it will be well, in view of its great importance, to illustrate the method of its manufacture.   .

104. Preparation and Properties. — Sulphuric acid is manufactured on the large scale by oxidizing sulphur dioxide in the presence of moisture thus : —

$$SO_2 + O + H_2O = H_2SO_4.$$

Oxygen from the air is used in oxidizing the dioxide. But sulphur dioxide cannot take up atmospheric oxygen directly.   There is a substance, however, that can unite directly with the oxygen of the air, and that is nitrogen dioxide, NO.   The reaction in this case is

$$NO + O = NO_2.$$
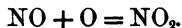
Now sulphur dioxide can take the atom of oxygen just taken from the air by the nitrogen dioxide thus : —

$$SO_2 + NO_2 = SO_3 + NO.$$
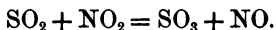
It will be noticed that the NO_2 has gone back to its original form, NO, and is again ready to take another atom of oxygen from the air, after which it will be able to oxidize another molecule of SO_2, when the same changes will be repeated in the same order an indefinite number of times.

But we had a molecule of SO_3.   This unites with a molecule of water thus : —

$$H_2O + SO_3 = H_2SO_4.$$
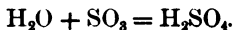
And so we have a molecule of sulphuric acid, and the history of this one molecule is the history of all.

Exp. 76. Fig. 25 shows an apparatus for making a small quantity of sulphuric acid. B is a generator containing copper filings and sulphuric acid to generate the sulphur dioxide. D is a tube leading from a bellows to supply the necessary air. C is a flask containing water to furnish steam. A contains copper filings and nitric acid to furnish the nitrogen dioxide. E is an escape-pipe for waste gases. G is a globe used as a
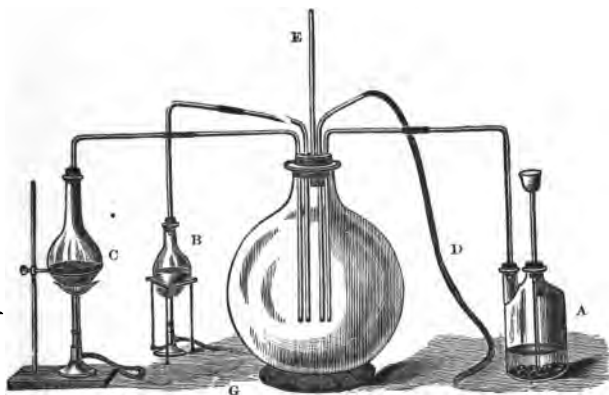
Fig. 25.

condensing-chamber. A clear glass carboy or large bottle will answer as well. It is perhaps needless to say that all the gases are delivered into the globe simultaneously, and that farther directions for manipulation are unnecessary.

In actual practice the manufacturer varies the details of the foregoing description but slightly. He generates the sulphur dioxide by roasting pyrites or by burning crude sulphur. The steam is generated in a boiler, and lead-lined

chambers are used for condensing purposes. Sometimes nitric acid is used in place of the nitrogen dioxide. This acid is generated from sodium nitrate and sulphuric acid, as previously explained. In this case what takes place may be represented by the following equation: —

$$2\,HNO_3 + 3\,SO_2 + 2\,H_2O = 3\,H_2SO_4 + 2\,NO.$$

Of course it is impossible to tell precisely what the exact changes are, or in what order they occur, but as to the final results there can be no doubt. It will be noticed that nitrogen dioxide, NO, also appears when the nitric acid is used.

The acid formed in the leaden chambers is weak, having a specific gravity of 1.55. It is concentrated in leaden pans until it reaches a specific gravity of 1.71, when it is withdrawn and further concentrated and purified in glass or platinum stills until its specific gravity is 1.84, when it is ready for the market.

Exp. 77.   Moisten a pine splinter with strong sulphuric acid. What occurs ?   Thus try a lump of sugar and a grain of starch.

Sulphuric acid chars vegetable substances. It abstracts water, or at least hydrogen and oxygen. This acid eagerly absorbs moisture, and thereby becomes dilute. When the union is taking place, much heat is evolved; therefore it should be an unvarying rule when diluting sulphuric acid to add the acid to the water, and not the water to the acid.

The uses of sulphuric acid in the manufactures are many and important. Thus it is used in bleaching factories, in soda factories, in paper mills, and in manufacturing artificial fertilizers and in many other important operations.

NORDHAUSEN OR FUMING SULPHURIC ACID, H_2SO_4, SO_3.

105. Fuming sulphuric acid is made by distilling ferrous sulphate containing but one molecule of water : —

$$4\,FeSO_4 + H_2O = 2\,Fe_2O_3 + 2\,SO_2 + H_2SO_4, SO_3.$$
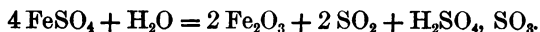
This acid is used in dissolving indigo in the process of dyeing Saxony blue, and in making the coal-tar colors. It is converted by means of water into ordinary sulphuric acid with the evolution of much heat.

106. Tests for Sulphuric Acid and the Sulphates. — 1. Free sulphuric acid or a soluble sulphate in solution is tested by adding barium chloride, $BaCl_2$, which throws down the white insoluble precipitate, barium sulphate, $BaSO_4$. Add hydrochloric acid to test the solubility of the precipitate.

2. An insoluble sulphate is fused on charcoal with sodium carbonate, the fused mass placed on a silver coin and moistened : a black spot is obtained. Now fuse a fresh portion of the substance with sodium carbonate on porcelain, place on silver and moisten : no black spot is obtained if the substance is a sulphate.

107. Tests for the Thiosulphates. — If not in solution, dissolve the substance in water and add hydrochloric acid : a white precipitate of sulphur is obtained, and sulphur dioxide set free if a thiosulphate be present.

SULPHUR AND CARBON.

108. Carbon Disulphide, CS_2, is the only known compound of sulphur and carbon. It is prepared by passing vaporized sulphur over charcoal heated to redness in a cylinder.

This substance is a limpid liquid in its pure form and

possesses a pleasant ethereal odor.   But in an impure state
it is colored and possesses a powerful, sickening odor.   Its
fumes are poisonous ; hence it is much used for destroying
vermin and as an insecticide.   In optics it is used for fill-
ing prisms, while in the arts it is used as a solvent for
rubber gum.   Its use in the laboratory has already been
exemplified.

The odor of the disulphide will serve as a test.

SELENIUM AND TELLURIUM.

109. Selenium: Symbol, Se ; Atomic Weight, 79 ; Specific
Gravity, 4.3. — Selenium is a rare element closely resem-
bling sulphur.   Berzelius discovered it in 1817 in the resi-
due collected from the sulphuric acid chambers at Gripsholm.
In a finely divided state and viewed by transmitted light,
selenium has a reddish color.   It exists in three modifica-
tions : viz. amorphous, vitreous, and crystalline selenium.

110. Tellurium: Symbol, Te ; Atomic Weight, 128 ; Spe-
cific Gravity, 6.24. — Tellurium is a rare element.   It is
a brittle, bluish white solid, possessing a decided metallic
lustre.   In its chemical compounds it resembles selenium
and sulphur.   The following table, given simply for in-
spection, will reveal how closely related these three ele-
ments are.

	Atomic Weight.	Specific Gravity.	Some Compounds.			
Sulphur	32	2.05	H_2S	SO_2	SO_3	H_2SO_4
Selenium. . . .	79	4.30	H_2Se	SeO_2	SeO_3	H_2SeO_4
Tellurium . . .	128	6.24	H_2Te	TeO_2	TeO_3	H_2TeO_4

EXERCISES.

(*For Review or Advanced Course.*)

1. How much sulphur would be required to produce 82 pounds of sulphuric acid ?

2. Test a piece of vulcanized rubber for sulphur by fusing with sodium carbonate, etc.

3. Test a sample of drinking-water for a sulphate.

4. Place some iron filings in a test-tube ; add dilute sulphuric acid, and heat gently. What gas is given off ? (SUG. Test with a match flame.) Evaporate the contents of the tube to dryness in an evaporating-dish after the iron has dissolved, and test the residue for a sulphate. What substances were obtained ? Write the equation.

5. How can you distinguish between a sulphite and a thiosulphate ?

6. What impurities would one expect to find in commercial sulphuric acid, when the material employed and the process of manufacture are taken into consideration ?

CHAPTER VIII.

SILICON, BORON, AND PHOSPHORUS, AND THEIR COMPOUNDS.

DATA FOR COMPUTATIONS. — SILICON : Symbol, Si ; Atomic Weight, 28 ; Specific Gravity, 2.49. — BORON : Symbol, B ; Atomic Weight, 11 ; Specific Gravity, 2.5. — PHOSPHORUS : Symbol, P ; Atomic Weight, 31 ; Specific Gravity, 1.83.

SILICON.

111. Occurrence, etc. — Silicon is a very abundant element, which, however, never occurs free. It forms from 22.8 to 36.2 per cent of the earth's crust. With oxygen it forms the abundant compound, silica, SiO_2. Silica is known to us in many different forms. Thus sand, sandstone, quartz, quartzite, agate, opal, chalcedony, flint, chert, and hone-stone are almost pure silica. They owe their different appearances sometimes to traces of coloring-matter, and sometimes to their physical conditions only. Tripoli consists of the minute, siliceous shells of microscopic plants, the diatoms. Siliceous conglomerates are coarse pebbles that have been joined by deposited silica. The silicates, such as feldspar, mica, and certain clays, are also silicon compounds.

Silicon is not used in the arts, and its preparation may be omitted. It has been obtained in three modifications, — amorphous, graphitoidal, and crystalline.

Of its compounds there are many. Silica is the most abundant. The silicates are a series of compounds of very complex constitution not very well understood. Orthosilicic

acid, H_4SiO_4, has not been separated. Silicon unites with hydrogen to form the compound, SiH_4, which somewhat resembles a gaseous compound formed by phosphorus and hydrogen, in that it is spontaneously inflammable.

112. Tests for Silicon Compounds. — Natural forms of silica, as quartz, etc., are readily recognizable by their physical properties.

2. Silicates in solution are first acidulated with hydrochloric acid, and then carefully evaporated to dryness. The dry mass is then dissolved in hydrochloric acid. If a silicate was present, it will now be reduced to a white insoluble powder, SiO_2, which is insoluble in acids, but soluble in potassium hydroxide, KOH.

3. An insoluble silicate is first fused with sodium carbonate on charcoal and then treated as in 2.

BORON.

113. Occurrence, etc. — Boron is a quite plentiful element which occurs only in compounds. The principal boron compounds are boric acid, H_3BO_3; borax, $Na_2B_4O_7 + 10\ H_2O$; and boracite, $2\ Mg_3B_8O_{15}$, $MgCl_2$.

Boric acid occurs in the waters of certain lagoons in Tuscany. Close by are jets of volcanic steam which are employed to evaporate the water, from which crystalline boric acid is deposited. The acid is purified by recrystallization.

California has several beds of native borax. These beds are on the sites of ancient lakes, long since dried up. Boric acid is obtained from this borax by treatment with hydrochloric acid, after which the boric acid is obtained by crystallization.

114. Tests for Boric Acid and its Compounds. — 1. Free
boric acid is detected in solutions by dipping in it a strip
of turmeric paper. The strip, when dried, turns brown,
and this color is not affected by dilute hydrochloric acid.
Alkalies also affect the color of this paper, but hydrochloric acid changes the color produced.

2. A borate may be treated with hydrochloric acid,
which frees boric acid. The next step is the same as in 1.

3. A solid borate may be tested by the flame test thus :
Make a bead of the substance on a loop of platinum wire
and strongly ignite in the Bunsen flame. Now moisten the
bead with sulphuric acid and ignite again. Finally moisten
the bead with glycerine and heat strongly : a green flame
is produced.

PHOSPHORUS.

115. Occurrence, etc. — Phosphorus is an element which
occurs widely distributed, but never in the free state. It
occurs in the older igneous rocks, from which all our fertile soils are derived. It forms with calcium the minerals
phosphorite, $Ca_3(PO_4)_2$, and apatite, $3\,Ca_3(PO_4)_2 + CaFCl$.
With iron it forms vivianite, $Fe_3(PO_4)_2 + 8\,H_2O$. Sombrerite, an impure form of calcium phosphate, furnishes a part
of the phosphorus of commerce. But most of our phosphorus is obtained from bones. Animals obtain phosphorus
from plants, and plants get it from the soil.

Phosphorus is prepared from bone-ash. The first step
is to convert the ash into acid calcium phosphate, which is
accomplished by using sulphuric acid : —

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 = CaH_4(PO_4)_2 + 2\,CaSO_4.$$
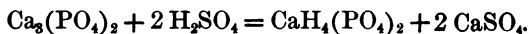
The solution of acid phosphate is evaporated to dryness
and ignited, when calcium metaphosphate is obtained : —

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2\,H_2O.$$
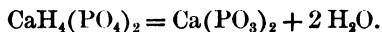
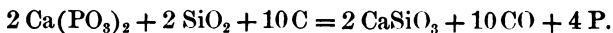The metaphosphate is now mixed with sand and charcoal, and put in earthen retorts that are placed in tiers in a furnace, and so arranged that their necks extend outside and dip under water (Fig. 26). When heat is applied, phosphorus is liberated, thus : —

$$2\,Ca(PO_3)_2 + 2\,SiO_2 + 10\,C = 2\,CaSiO_3 + 10\,CO + 4\,P.$$

The phosphorus thus obtained is melted under water, and strained through chamois leather, to remove coarse impurities : it is further purified by treating it with sulphuric acid and potassium dichromate, when it is cast in sticks of the form found in market.

Fig. 26.

In addition to the ordinary waxy form of phosphorus found in the ordinary sticks of commerce, two other modifications are known. When common phosphorus is dissolved in carbon disulphide and the solution is allowed to evaporate slowly, octahedral crystals are obtained. Again, when ordinary or crystalline phosphorus is heated to 240° C. in the absence of oxygen, red or amorphous phosphorus is obtained.

Phosphorus is a highly inflammable substance, igniting at low temperatures. In consequence of this property it
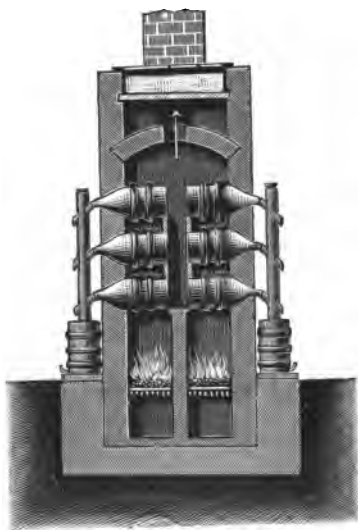
is used in large quantities as an ingredient of match-tips. The inflammable nature of phosphorus may be safely shown thus : —

EXP. 78.   Place in a test-tube a bit of phosphorus as large as a kernel of wheat.   Dissolve in carbon disulphide, and pour the solution over a piece of filter-paper.   Place the paper on a metallic support, and in a short time the disulphide will evaporate, leaving the phosphorus in a finely divided state, and the paper will soon ignite spontaneously.

Phosphorus is a substance that should be handled with care.   It should always be taken up with a pair of pincers and should be cut under water.   Upon the flesh its burns produce deep and dangerous wounds, often penetrating to the bone.

The peculiar odor and the physical characteristics of phosphorus serve to identify it.

PHOSPHORUS AND HYDROGEN.

116.   Phosphorus and hydrogen form three compounds which are respectively, gaseous, liquid, and solid substances: PH_3, PH_2, and $P_2H(?)$.   The first of these is often called *phosphine*, and its preparation will be given. None of these compounds are of great importance to the beginner.

EXP. 79.   Place in a generating-flask (Fig. 27) a strong solution of potassium hydroxide.   Drop in a few small pieces of phosphorus; and, lastly, add a small quantity of ether, for the purpose of expelling the air from the apparatus.   Insert the delivery-tube, heat gently, and allow the bubbles of phosphine to come up through the water.   On striking the air, the gas will be found to be spontaneously inflammable, forming by its

combustion rings of phosphorus pentoxide having a peculiar vortex motion. The formation of the gas is as follows : —

$$4\,P + 3\,KOH + 3\,H_2O = 3\,KH_2PO_2 + PH_3.$$

PHOSPHORUS AND OXYGEN.

117. There are two oxides of phosphorus: viz. P_2O_3 and P_2O_5. The first is obtained when phosphorus is burned in
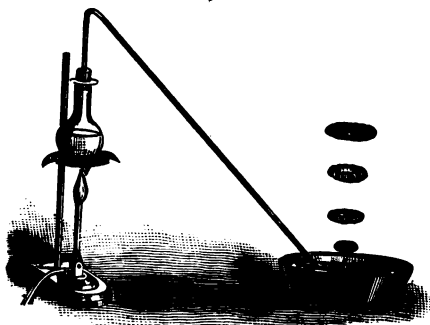
FIG. 27.

a limited supply of air, and the second when the air-supply is not limited. These oxides are the anhydrides of phosphorous and phosphoric acids.

THE PHOSPHOROUS OXACIDS.

118. There are three primary acids in this series and two others that are derived from phosphoric acid : —

Hypophosphorous acid	. . .	H_3PO_2.
Phosphorous acid	. . . . .	H_3PO_3.
Phosphoric acid	. . . . .	H_3PO_4.

When phosphoric acid is heated, water is driven out; and by employing suitable temperatures two derived acids are to be had: —

Metaphosphoric acid . . . . HPO_3.
Pyrophosphoric acid . . . . $H_4P_2O_7$.

The basicity of hypophosphorous and phosphorous acids merits notice. Hypophosphorous acid is monobasic, only giving up one of its hydrogen atoms. Its formula might, therefore, well be written, HH_2PO_2. Phosphorous acid is dibasic, and might be represented by the formula, H_2HPO_3. The potassium salts of these acids are, for example, KH_2PO_2 and K_2HPO_3.

Phosphoric acid merits further notice.

Exp. 80. Place a small quantity of red phosphorus in an evaporating-dish, and cover with reagent nitric acid. Warm gently, adding more nitric acid from time to time, until the phosphorus disappears and red fumes cease to come off. Now expel the excess of nitric acid by heating gently, when phosphoric acid is obtained as a syrupy liquid.

This is a tribasic acid which gives up one, two, or three of its hydrogen atoms. Its sodium salts serve as examples: NaH_2PO_4, Na_2HPO_4, Na_3PO_4.

119. Tests for Phosphoric Acid. — 1. To the solution to be tested add ammonia and ammonium chloride. A clear solution is obtained. Now add magnesium sulphate, $MgSO_4$, and a white crystalline precipitate, $MgNH_4PO_4$, is obtained, usually after standing some time.

2. Add silver nitrate to the solution to be tested. A light yellow precipitate is obtained, which is soluble in ammonia, nitric acid, and in acetic acid.

NOTE. Make both tests before reporting phosphoric acid, and also be sure that no arsenic acid is present.

EXERCISES.

(*For Review or Advanced Course.*)

1. Test a sample of drinking-water for silicates thus: Acidulate with hydrochloric acid one half-litre of the water to be tested. Now evaporate strictly to dryness. Again dissolve the residue in hydrochloric acid, and then examine the contents of the dish used for evaporating the water, for the white powder, SiO_2.

2. Collect some of the sediment from the bed of a small stream and examine with a microscope for the shells of diatoms.

3. Collect as many forms of silica as possible and describe each form.

4. Why are siliceous pebbles mostly rounded and smooth?

5. For what household purposes is borax used?

6. Burn a bit of bone and then dissolve the ash in hydrochloric acid. Now add ammonia, and note the precipitate of calcium phosphate.

7. Test the salts of several different acids for their acids. Does the salt give the test for the acid from which the salt was derived?

CHAPTER IX.

INTRODUCTORY TO THE METALS.

120. Properties of the Metals. — Formerly the elements were divided into two groups, — the Metals and the Non-metals. But it has become apparent that the distinction is not well founded. The elements form a series so closely graded in properties that it is difficult even to define a metal. But in general we may say that a metal is an element which possesses, when in a coherent condition, a peculiar lustre, termed a metallic lustre. Moreover, the oxides of the metals, excepting a very few of the higher ones, are not acid-forming.

The specific gravities of the metals vary from that of osmium, 22.48, to that of lithium, 0.59.

The specific heat of a metal is always less than unity. It has been found that when the specific heat of an element is multiplied by the atomic weight of that element a nearly constant quantity is obtained, viz. 6.4. This product is termed the atomic heat of an element. From an inspection of the results so obtained, Dulong and Petit announced the law: *The specific heat of an element varies inversely as the atomic weight of that element.*

While the law is but approximately true, it has nevertheless been utilized in determining the atomic weights of some of the rarer elements. In order to do this, the specific heat of the element was first determined. Some of its compounds were then analyzed, and that atomic weight

was selected which would give a product of about 6.4 when multiplied by the specific heat.

The melting-points of the metals vary widely. Thus mercury melts at $-40°$ C., while the most intense heat obtainable has not sufficed to melt osmium.

Metals unite in definite and in indefinite proportions to form *alloys*. Thus brass consists of zinc and copper in varying proportions. Pewter contains four parts tin and one part lead. Alloys are found extremely useful, since in them some particular requirement may be obtained which a single metal does not possess.

An *amalgam* is an alloy of a metal with mercury.

121. Classification of the Metals. — In the following pages the metals are classified according to some requirements in analytical work. The method of classification may be made clear by supposing a solution containing a salt of each of the common metals. To this solution *hydrochloric acid*, HCl, is to be added. With certain of these metals the acid forms insoluble chlorides. These metallic chlorides are accordingly precipitated and may be removed from the solution containing the remaining metals by filtration. The metals thus precipitated are called the

FIRST GROUP METALS.

Lead . . . . Pb.
Silver . . . . Ag.
Mercury . . . . Hg(ous).

If through the acid filtrate from which the first group metals have been removed, *sulphuretted hydrogen*, H_2S, now be passed, we obtain as precipitates, insoluble in dilute acids, the sulphides of the

SECOND GROUP METALS.

Arsenic . . . . As.
Antimony . . . . Sb.
Tin . . . . Sn.
Bismuth . . . . Bi.
Copper . . . . Cu.
Cadmium . . . . Cd.
Mercury . . . . Hg(ic).

These sulphides can now be filtered out, and by a little judicious treatment, to be explained further on, the filtrate is readily prepared for the separation of the next group. The third group metals are precipitated as hydroxides and sulphides insoluble in the presence of an alkali by adding *ammonia*, NH_3, *ammonium chloride*, NH_4Cl, and *ammonium sulphide*, $(NH_4)_2S$. Following are

THE THIRD GROUP METALS.

Iron . . . . Fe.
Chromium . . . . Cr.
Aluminum . . . . Al.
Nickel . . . . Ni.
Cobalt . . . . Co.
Manganese . . . . Mn.
Zinc . . . . Zn.

These metals, now in an insoluble compound, may be removed from the solution by filtration, and the filtrate by appropriate treatment may be made ready for the separation of the next group. In the fourth group the metals are precipitated as carbonates insoluble in alkalies by adding *ammonia*, NH_3, *ammonium chloride*, NH_4Cl, and *ammonium carbonate*, $(NH_4)_2CO_3$.

THE FOURTH GROUP METALS.

Barium	Ba.
Strontium . . , ...	Sr.
Calcium	Ca.
Magnesium	Mg.

NOTE. In practice, the magnesium is removed from the solution from which the carbonates of the first three metals of this group have been separated by adding *disodium phosphate*, Na_2HPO_4. This precipitates the magnesium as a double salt, magnesium ammonium phosphate, $MgNH_4PO_4$. Magnesium carbonate is soluble even in alkalies.

If now the insoluble compounds of the fourth group be removed by filtration, we have in the filtrate only the fifth group metals. These do not give precipitates with ordinary reagents. These are the

FIFTH GROUP METALS.

Potassium	K,
Sodium	Na,
and the radical Ammonium.	NH_4.

By following the plan just outlined, the metals are separated into groups. Now each of these groups can be taken up, and the individual metals therein can be separated from one another, as will be explained in appropriate places. This process of separation and identification is termed *Qualitative Analysis*. When the weights of the substances present in a compound are determined, the process is termed *Quantitative Analysis*.

We are now ready to study the metals in detail.

CHAPTER X.

THE FIRST GROUP METALS.

DATA FOR COMPUTATIONS. — LEAD: Symbol, Pb''; Atomic Weight, 207; Specific Heat, 0.0315; Melting-point, 334°; Specific Gravity, 11.37. — SILVER: Symbol, Ag'; Atomic Weight, 108; Specific Heat, 0.0570; Melting-point, 1000°; Specific Gravity, 10.53. — MERCURY: Symbol, Hg', ''; Atomic Weight, 200; Specific Heat, 0.0319; Melting-point, —40°; Boiling-point, 357.25°; Specific Gravity, 13.55.

LEAD.

122. Occurrence and Preparation. — Metallic lead occurs only in insignificant quantities. Its principal ore is galena, PbS, which occurs in dark, shining cubes, and in other forms belonging to the regular system. Nearly every ore of lead is argentiferous, *i.e.* silver bearing.
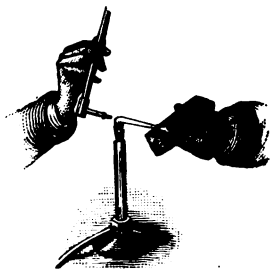

FIG. 28.

EXP. 81. Place a bit of galena (or a little of any compound containing lead) in a shallow cavity which has been prepared in a piece of charcoal (Fig. 28). Cover the substance with sodium carbonate, Na_2CO_3, and moisten with a few drops of water. Now heat the substance before the blow-pipe reducing flame. Bright metallic beads will be obtained. Test these beads thus: Place one on an anvil or on a piece of iron, and strike it lightly with a hammer. Is it malleable? Brittle? Cut one of the beads with a knife. Is it hard? Note the lustre of

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the beads, and draw one across a piece of white paper. Does it leave a streak?

Metallic lead is largely used in the arts. It is prepared by heating galena in a limited supply of air. Sometimes a reducing agent like coal-dust is used in its reduction.

Ex. Show how the preceding experiment illustrates these processes. Name the uses of metallic lead.

123. Properties and Compounds of Lead. — Lead is a silvery white metal which soon tarnishes in the air. It is much used for lead pipes. It is insoluble in pure water, but natural waters are never pure. Hence lead pipes should never be used for conveying water intended for drinking or for domestic purposes. Lead salts act upon the system as a virulent, cumulative poison.

Lead dissolves readily in nitric acid, forming the soluble salt, $Pb(NO_3)_2$. This salt and the acetate, $Pb(C_2H_3O_2)_2$, when dissolved in water make good solutions for laboratory practice.

Some of the compounds of lead are used in the arts. We notice the following:

(a) *Lead Oxide* or *Massicot*, PbO, is a yellow powder. *Litharge* is an impure form of lead oxide. These are prepared by heating lead in the air. Litharge is used in making flint glass and in glazing earthenware. *Red lead*, or *minium*, Pb_3O_4, is used as a pigment.

(b) *White lead* is a mixture of the carbonate and hydroxide of lead. This is the best white paint, and is prepared by the action of crude acetic acid on sheets of lead that are placed in earthen crocks and covered with manure or spent tan bark. The decomposing manure furnishes the carbon dioxide necessary to convert the acetate, first formed, into white lead.

(*c*) *Lead Acetate*, $Pb(C_2H_3O_2)_2$, is much used in medicine. It is also used as a reagent in the laboratory. It may be obtained by the action of acetic acid on metallic lead. Lead acetate is used in dyeing, as shown in the following experiment : —

EXP. 82. Moisten a strip of white cotton cloth in a solution of lead acetate. Now moisten in potassium dichromate solution, $K_2Cr_2O_7$. What color is the strip dyed ?

(*d*) *Lead Chloride*, $PbCl_2$, is a precipitate met with in the course of analysis. It is a white crystalline substance, soluble in hot water.

(*e*) *Chrome Yellow*, $PbCrO_4$, is used as a pigment. It is obtained when potassium dichromate is added to a soluble lead salt.

124. Tests for Lead. — 1. Metallic lead is recognized by its physical properties, or the metal is dissolved in nitric acid and tested as in 2.

2. Lead in a solution of its salts is recognized by the color of its precipitates : —

$K_2Cr_2O_7$ gives $PbCrO_4$, yellow.
KI gives PbI_2, yellow scales.
H_2SO_4 gives $PbSO_4$, white.
H_2S gives PbS, black.

3. A solid may be tested before the blow-pipe. The beads obtained are then dissolved in nitric acid and tested by 2.

SILVER.

125. Occurrence and Preparation. — Native metallic silver occurs in considerable quantities along with native copper deposits. Most of the silver of commerce comes, however,

from the lead-furnaces. There are some ores of silver such as argentite, Ag_2S, and horn silver, $AgCl$. Silver also occurs in connection with other metals and combined with arsenic and sulphur.

Exp. 83. Place a zinc strip in a test-tube containing a solution of silver nitrate. Note the dark deposit that soon collects on the zinc, and then remove it to a piece of charcoal, and heat it before the blow-pipe. Try the bead as you tried lead. Complete this equation : —

$$2\,AgNO_3 + Zn = 2\,Ag + \cdots.$$
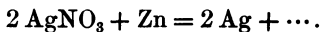
Exp. 84. Add hydrochloric acid to a solution of silver nitrate. Collect the precipitate, $AgCl$, on charcoal, and heat in the blow-pipe flame. Do you obtain a silver bead?

Silver is obtained from the lead-furnaces according to the following process: The silver is present in the lead ores in very small quantities. But the same process that reduces the lead also reduces the silver. Now the lead is allowed to cool in large tanks. During the cooling process pure crystals of lead separate out, and these are removed. By repeating this process, an alloy is obtained at last that is rich in silver.

This alloy is now heated in bone-ash vessels, called "cupels," over which a current of air is passing. In this way the lead is oxidized and absorbed by the cupels, leaving pure silver. This process is called *cupellation.*

Other processes of reducing silver, of less importance to the beginner, are also employed to some extent.

126. Properties and Compounds. — Silver has long been esteemed as one of the precious metals. It is a bright metal that does not oxidize in the air at any temperature ; hence its use for jewelry and coinage. Some substances like sulphur, chlorine, bromine, etc., cause silver to tarnish.

Ex. Why do coins carried in the pockets with matches, blacken. Explain the tarnishing of egg-spoons and mustard-spoons. Why should silver drinking-cups not be used at sulphur springs ? Name the uses of silver.

Silver dissolves rapidly in nitric acid, affording silver nitrate, $AgNO_3$. This salt is much used as a reagent, and is the best one for working purposes in the laboratory.

Some of the compounds of silver are : —

(a) *Silver Nitrate*, or *Lunar Caustic*, $AgNO_3$. This salt has just been mentioned. It is used in medicine and in photography.

(b) *Silver Chloride*, AgCl, is the precipitate obtained by adding the group reagent, HCl, to a solution of a silver salt. It is soluble in ammonia.

(c) A silver-plating solution can be prepared thus : Precipitate silver nitrate with a solution of common salt, NaCl. Filter, and wash the precipitate quickly in pure water. Now dissolve the precipitate in an excess of potassium cyanide, KCN, when the solution is ready for use. These equations explain the steps involved : —

$$AgNO_3 + NaCl = AgCl + NaNO_3;$$
$$AgCl + 2\,KCN = \underline{AgCN, KCN} + KCl.$$
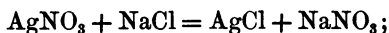
127. Tests for Silver. — Metallic silver is recognized by its physical properties. But it may be dissolved in nitric acid, and identified as in 2.

2. Silver in solutions of its salts may be recognized by the color of its precipitates as follows : —

Hydrochloric acid, HCl, gives AgCl, white (sol. in ammonia).
Potassium dichromate, $K_2Cr_2O_7$, gives $AgCrO_4$, red.
Hydrogen sulphide, H_2S, gives Ag_2S, black.
Potassium iodide, KI, gives AgI, light yellow.

3. A solid may be reduced before the blow-pipe, and the bead dissolved in nitric acid, and tested as in 2.

MERCURY.

128. Occurrence and Preparation. — Mercury occurs free in small drops disseminated through its principal ore, cinnabar, HgS. The artificial sulphide is known as the pigment *vermilion*.

EXP. 85. Place a bit of cinnabar in a hard glass tube open at both ends. Hold the tube somewhat slanting in the Bunsen flame, and heat strongly. Note the fumes escaping from the upper end of the tube. Also note the metallic mirror formed on the sides of the tube a short distance above the cinnabar. The reaction is : —

$$HgS + O_2 = Hg + SO_2.$$
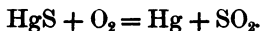
The preparation of mercury for commerce is a very simple operation. The ore, cinnabar, is simply heated in a current of air. The sulphur is oxidized to the dioxide, and mercury is set free in the form of vapors which are condensed in suitable condensers.

129. Properties and Compounds. — Mercury is a silver-white liquid which slowly passes into a vapor at all temperatures between its freezing-point and boiling-point. It is largely used in making philosophical instruments and in making amalgams. On the system, the vapors of mercury act as a poison. This metal has been known since the highest antiquity, and its compounds have been largely utilized. The most common compounds of mercury are : —

(*a*) *Red Oxide of Mercury*, HgO, is used in medicine. It is prepared by heating a mixture of mercury and mercuric nitrate until red fumes cease to come off. When sodium or potassium hydroxide is added to a salt of mercury, the same oxide is obtained, but the color is yellow in this case.

(b) *Mercurous Chloride*, or *Calomel*, Hg_2Cl_2, is used in medicine. It is prepared by subliming an intimate mixture of mercuric chloride and mercury. It is also obtained as a group precipitate when hydrochloric acid is added to a soluble mercurous salt. This precipitate turns black when moistened with ammonia. It is soluble in nitro-hydrochloric acid.

(c) *Mercuric Chloride*, or *Corrosive Sublimate*, $HgCl_2$, is a deadly poison. It is used in the laboratory as a reagent. It is prepared by subliming a mixture of mercuric sulphate and common salt: —

$$HgSO_4 + 2\,NaCl = HgCl_2 + Na_2SO_4.$$
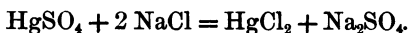
(d) *Mercurous Nitrate*, $Hg_2(NO_3)_2$, is prepared by acting on an excess of metallic mercury with cold dilute nitric acid. If the acid be in excess, mercuric nitrate, $Hg(NO_3)_2$, is formed. Mercurous nitrate is a good working compound for laboratory purposes.

It will be noticed that mercury forms two compounds with hydrochloric acid, Hg_2Cl_2 and $HgCl_2$; also two compounds with nitric acid are to be had, $Hg_2(NO_3)_2$ and $Hg(NO_3)_2$. These compounds are called respectively mercu*rous* and mercu*ric* salts. If we were to examine all the compounds of mercury, we should find that with every acid two salts are formed. These would correspond to the mercurous and mercuric salts formed with hydrochloric and nitric acids. Those compounds containing the least proportion of the acid constituent are called mercu*rous* compounds, while those with the greater proportion of the acid are the mercu*ric* compounds.

It will be noticed that in the mercurous salts two atoms of mercury appear. These taken together are equivalent to a diad, while in the mercuric compounds one atom is a

diad. It is customary to write all mercurous compounds with an even number of atoms. Mercurous salts only are precipitated in the first group.

Besides mercury there are other metals which form two classes of compounds, iron, tin, and copper being the most prominent.

130. Tests for Mercury. — 1. Metallic mercury is readily recognized by its physical properties.

2. Mercury in solutions of *mercurous* salts is detected by adding hydrochloric acid, which gives the white precipitate, Hg_2Cl_2. This precipitate turns black by the addition of ammonia.

3. Mercury in solutions of mercuric salts is tested by adding stannous chloride, $SnCl_2$. At first a white precipitate, Hg_2Cl_2, is formed, which changes to gray, and finally to black. By warming this precipitate and rubbing it with a glass rod, minute beads of metallic mercury may be obtained. It usually requires some time for these changes to take place in this precipitate. The action of the tin salt is as follows : —

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg.$$
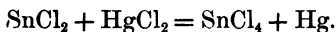
4. If a clean copper wire be introduced into a solution of either a mercurous or a mercuric salt, a coating of metallic mercury is obtained on the wire.

131. Separation and Identification of the First Group Metals. — As previously explained, the first group metals are separated from all others by adding hydrochloric acid to a solution containing salts of these metals. The chlorides, $PbCl_2$, $AgCl$, and Hg_2Cl_2, are thus obtained as a precipitate. These insoluble chlorides are now filtered out, and as they lie on the filter-paper, washed by pouring over them a *little*

cold water. This leaves them clean and still lying on the filter-paper. Now proceed by 1.

1. Add much hot water to the chlorides. Lead chloride alone is dissolved, and the solution runs through the filter-paper, and is to be collected in a suitable dish, such as a small beaker-glass. Now test this solution by Art. 124, 2. In this way the lead is identified. Now proceed by 2.

2. The chlorides of silver and mercury remain on the filter-paper. So add ammonia, and thus dissolve the silver chloride. Save the filtrate as before, and turn it back on the filter-paper once or twice to insure the complete solution of the silver chloride. Now to the filtrate add nitric acid to an acid reaction with blue litmus paper. The silver will be again precipitated as AgCl. In this connection this precipitate is a sufficient guarantee of the presence of silver. But if the precipitate be plentiful, it may be collected on charcoal and reduced to a silver bead before the blow-pipe. Now proceed by 3.

3. At the same time the silver chloride was dissolved in ammonia, the mercurous chloride was turned black by the action of the ammonia. No further identification of the mercury is necessary in this connection. If the student so desires, he may dissolve this black precipitate in nitrohydrochloric acid and test it by adding $SnCl_2$, Art. 130, 3.

GENERAL NOTE. Since lead chloride dissolves so easily, some lead always goes over into the second group. It is necessary that the solution be *cold* when the hydrochloric acid is added.

EXERCISES.

(For Review or Advanced Course.)

1. Compute the atomic heat of lead, of silver, and of mercury.

2. Arrange the formulæ of all the acids previously studied in a vertical column at the left side of a sheet of paper. At the right of each acid write

the formula of the salt which that acid forms with lead. At the right of the lead salts write the formulæ of the silver salts. Make two columns for mercury, and in the first write the mercurous salts, and in the second write the mercuric salts. Now name all the salts written.

3. Write the equation for the solution of metallic lead in nitric acid, knowing that $Pb(NO_3)_2$, NO, and H_2O are the products of the reaction.

4. Write the reactions for hydrochloric acid and the following salts : $Pb(NO_3)_2$, $AgNO_3$, and $Hg_2(NO_2)_2$.

5. Try the effect of a strip of zinc on a solution of a salt of lead ; upon a salt of mercury. Write the reactions.

CHAPTER XI.

THE SECOND GROUP METALS.

DATA FOR COMPUTATIONS. — ARSENIC: Symbol, As$'''$, ^{v}; Atomic Weight, 75; Specific Heat, 0.0822; Melting-point, 356°; Specific Gravity, 5.73. — ANTIMONY: Symbol, Sb$'''$, ^{v}; Atomic Weight, 120; Specific Heat, 0.0523; Melting-point, 425°; Specific Gravity, 6.71. — TIN: Symbol, Sn$''$, $''''$; Atomic Weight, 118; Specific Heat, 0.0548; Melting-point, 230°; Specific Gravity, 7.29. — BISMUTH: Symbol, Bi$'''$; Atomic Weight, 210; Specific Heat, 0.0305; Melting-point, 270°; Specific Gravity, 9.80. — COPPER: Symbol, Cu$'$, $''$; Atomic Weight, 63; Specific Heat, 0.0952; Melting-point, 1090°; Specific Gravity, 8.95. — CADMIUM: Symbol, Cd$''$; Atomic Weight, 112; Specific Heat, 0.0567; Melting-point, 315°; Specific Gravity, 8.60.

132. *The second group* metals yield sulphides insoluble in dilute acids. These sulphides are obtained from solutions after the removal of the first group metals, as previously explained. Since the sulphides of arsenic, antimony, and tin are soluble in yellow ammonium sulphide, $(NH_4)_2S$, these metals may be regarded as forming a subgroup, and in analysis they are separated from bismuth, copper, and cadmium by the addition of this reagent to the sulphides of the whole group.

ARSENIC.

133. Occurrence and Preparation. — Metallic arsenic occurs native in kidney-shaped masses of a laminated structure. But most of our arsenic is prepared from the ores, orpiment, As_2S_3, and mispickel, $(FeS)_2As$.

Exp. 86. Make a pellet of arsenic trioxide, As_2O_3, with powdered charcoal and a drop or two of water. Place the pellet in the bottom of a hard glass test-tube, and heat gently, to expel the moisture. Now drop into the tube a loosely fitting cork of chalk, and then heat the pellet strongly. Note the deposit of arsenic on the sides of the tube above the chalk.

Arsenic is prepared for commerce by heating its ores in earthen tubes. The vapors of arsenic are condensed in iron condensers. The arsenic thus obtained is purified by subliming it with charcoal. As thus prepared it forms rhombohedral crystals possessing a bright metallic lustre.

134. Properties and Compounds. — Arsenic is a bright solid which oxidizes quite readily in warm, moist air, forming a dark substance known as fly-powder. Under ordinary pressures, arsenic seems to vaporize without melting, at 356°. Under greater pressure it may be obtained in the liquid form.

Both arsenic and its soluble compounds act as deadly poisons when taken into the system. It matters not whether the arsenic be taken internally or whether it be absorbed by the lungs or through the pores of the skin in the form of dust or vapor, the action is the same. Wallpaper or carpets colored with arsenic compounds are almost certain to bring on the symptoms of arsenic poisoning.

Arsenic stands midway in its properties between the metals and the non-metals. In its chemical compounds it is closely allied to phosphorus, while in its physical properties it resembles antimony.

The metal arsenic can be brought into solution by treating it with nitro-hydrochloric acid or with chlorine water. Arsenic acid is thus obtained : —

$$2\,As + 5\,Cl_2 + 8\,H_2O = 2\,H_3AsO_4 + 10\,HCl.$$
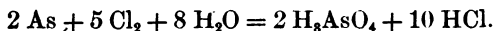
Arsenic trioxide, As_2O_3, is soluble in potassium or sodium hydroxide, thus : —

$$As_2O_3 + 6\,NaOH = 2\,Na_3AsO_3 + 3\,H_2O + \text{an excess of NaOH.}$$
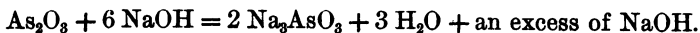
The sodium arsenite thus formed is soluble in water.

Some of the compounds of arsenic follow : —

(*a*) *Arsenic Trioxide*, As_2O_3, is a white substance usually sold in drug stores under the name "arsenic." It is used in medicine and in taxidermy. It is supposed to be the anhydride of *Arsenious Acid*, H_3AsO_3, which has not been isolated. The arsenites are known.

(*b*) *Scheele's Green* or *Copper Arsenite*, $CuHAsO_3$, and *Schweinfurth's Green* or *Copper Aceto-arsenite*, $(CuOAs_2O_3)_3$, $Cu(C_2H_3O_2)_2$ are used as pigments, and both are sold under the name "Paris green." These substances as well as London purple, another somewhat similar compound of copper and arsenic, are extensively used as insecticides.

(*c*) *Arsenic Pentoxide*, As_2O_5, may be considered to be the anhydride of *Arsenic Acid*, H_3AsO_4. The pentoxide is to be had by treating arsenic with strong nitric acid. Arsenic acid has already been mentioned.

(*d*) *Arsenious Sulphide*, As_2S_3, is the precipitate obtained in the regular course of analysis. It is soluble in yellow ammonium sulphide.

135. Tests for Arsenic. — 1. A solid substance containing arsenic, when heated on charcoal before the blow-pipe reducing flame, yields vapors having an odor resembling garlic.

2. When hydrogen sulphide is passed through a solution containing arsenic, the yellow precipitate, As_2S_3, is obtained.

3. A solid or a solution is best tested for arsenic by the spot-test, thus : The substance supposed to contain arsenic

is placed in an evaporating-dish, and a crystal of potassium chlorate and hydrochloric acid are added. Heat is now applied, when the arsenic, if any be present, is oxidized to arsenic acid. The boiling is continued until the excess of chlorine is driven off.

In a generating-flask place some arsenic-free zinc, and water. Add sulphuric acid, and if hydrogen gas is not freely given off, add a crystal of pure copper sulphate, which will cause a copious evolution of hydrogen. As soon as the apparatus is free from air, add the solution to be tested as now prepared in the evaporating-dish. Immediately insert a jet delivery-tube and ignite the stream of escaping gas, AsH_3, and direct the flame against a cold porcelain surface. If arsenic be present, a steel-gray spot or mirror will be obtained on the porcelain. Make several spots, and make sure that they are arsenic, thus : —

(*a*) Test one of the spots with yellow ammonium sulphide ; it turns yellow.

(*b*) Test another with a drop of hydrochloric acid ; *it does not dissolve.*

(*c*) Add to another a drop of a solution made by adding potassium hydroxide to chlorine water ; it dissolves.

(*d*) Treat another with hot nitric acid ; it dissolves clear. Add to this solution a drop of silver nitrate ; no change in color occurs. Now place the tip of a blow-pipe at the mouth of an uncorked ammonia bottle and force a stream of ammonia gas against the same solution ; it turns *brick-red* or *yellow*. You are now certain that arsenic in some form is present.

4. An arsenate can be distinguished from an arsenite, thus : To the solution to be tested add magnesium sulphate, $MgSO_4$. A precipitate may be either an arsenate or

an arsenite.   Now add ammonia and ammonium chloride.
If the precipitate dissolves, it is an arsenite ; if it does not
dissolve, it is an arsenate.

NOTE.   Be sure that phosphates are absent before applying this test.

ANTIMONY.

136. Occurrence and Preparation. — Metallic antimony
occurs in small scaly masses, which also contain as impuri-
ties, iron, silver, etc.   But the chief source of antimony is
the ore, stibnite, Sb_2S_3.

EXP. 87.   Make a pellet of any antimony compound with
sodium carbonate, and moisten with a drop of water.   Place
the pellet on charcoal, and heat before the reducing blow-pipe
flame.   A bright bead is obtained.   Test this bead as in the
case of lead.

Antimony is prepared for commerce by heating stibnite
in vessels with perforated bottoms.   The sulphide melts and
runs through pure.   It is next heated with metallic iron,
which unites with the sulphur and sets the antimony free.

137. Properties and Compounds. — Antimony is a bluish
white metal, so brittle that it may be ground to a dust.
It is used principally in making alloys, to which it imparts
hardness and the property of expanding when cooling.
Large quantities of antimony are used in making type
metal.   Antimony is also used in some pharmaceutical
preparations.

With acids antimony forms salts, in which it acts like a
trivalent metal as in antimony trichloride, $SbCl_3$.   The
group, SbO, forms basic salts, in which it acts as a monad.
The salts thus formed are called *antimonyl* salts.   Anti-
monyl sulphate, $(SbO)_2SO_4$, will serve as an example.

Antimony also acts like an acid-forming element. Antimonic acid, H_3SbO_4, is the principal antimony acid. This acid closely resembles phosphoric and arsenic acids.

Hot nitro-hydrochloric acid dissolves metallic antimony, yielding antimony trichloride, $SbCl_3$. When dissolved in water acidulated with hydrochloric acid, this chloride makes a good working solution for laboratory practice.

Some of the antimony compounds follow: —

(a) The oxides, Sb_2O_3, Sb_2O_4, and Sb_2O_5, give rise to a series of acids similar to those of phosphorus.

(b) *Tartar Emetic*, $C_4H_4KSbO_7$, is used in medicine. It is prepared by dissolving antimony trioxide in potassium tartrate, $KHC_4H_4O_6$.

(c) *Antimony Trisulphide*, Sb_2S_3, is the orange-colored precipitate obtained in the course of analysis. It is soluble in yellow ammonium sulphide.

138. Tests for Antimony. — 1. Any antimony compound when heated on charcoal with sodium carbonate yields a bright, brittle bead of metallic antimony.

2. Any solution of an antimony salt gives with hydrogen sulphide an orange-colored precipitate, Sb_2S_3.

3. Antimony compounds may be placed in a generating-flask with zinc and sulphuric acid, and the escaping gas, SbH_3, may be ignited as soon as the apparatus is free from air and the flame directed against a cold porcelain surface. Black or velvety brown spots of antimony are obtained. These spots may be distinguished from arsenic thus: —

(a) An antimony spot with yellow ammonium sulphide turns *orange*.

(b) With hot nitric acid it turns *white*.

(c) With a drop of a solution of potassium hydroxide in chlorine water it is *insoluble*.

(*d*) The white spot formed in (*b*), when treated with silver nitrate and ammonia vapor, gives no color; but when a drop of ammonia solution is added, it turns *black*.

TIN.

139. Occurrence and Preparation. — But small quantities of tin occur native. Commercial tin is obtained from the ore, tin stone or cassiterite, SnO_2. This ore occurs in veins in the older schistose and crystalline rocks. It is also found in nodules in the beds of rivers flowing through these regions. As thus found it is popularly called " stream tin." The oldest tin mines are in Cornwall, England, but it is now mined in Australia, Bolivia, Peru, and in the Black Hills in South Dakota.

Exp. 88.   Make a paste of a tin compound with solid potassium cyanide and a drop of water. Heat this paste on charcoal in the reducing flame. Small beads of tin are obtained with great difficulty. If the oxidizing flame be used, a coating of stannic oxide will be formed around the assay, which is pale yellow while hot and white when cold.

In the commercial preparation of tin, the tin stone is first crushed fine and then washed to remove some of the impurities. It is then further purified by roasting it in revolving inclined cylinders through which a blast of air is passing. In this way volatile substances, such as arsenic and sulphur, are driven off while other impurities are oxidized. The ore is now washed again and thus obtained quite pure. The pure ore is now mixed with anthracite coal and reduced in a blast-furnace. The tin thus obtained is now drawn off and purified by liquation; *i.e.* it is gradually melted in a reverberatory furnace. Since the pure

tin is more fusible than its alloys, it melts first, and is drawn off and stirred with poles of green wood; a dross separates, thus leaving the tin in a state of great purity.

140. Properties and Compounds of Tin. — Tin is a white, malleable metal, the lustre of which is quite permanent in the air at ordinary temperatures. It is extensively used as tin foil and for coating thin sheets of iron to form tin plate. When alloyed with lead, solder is formed.

Tin as a base forms two series of salts, the stannous and the stannic compounds. It also forms acids of small importance.

Tin reacts with hydrochloric acid to form stannous chloride, $SnCl_2$. With nitro-hydrochloric acid containing an excess of hydrochloric acid, stannic chloride, $SnCl_4$, is obtained. Solutions of these salts are useful for laboratory practice.

Some of the compounds of tin follow: —

(*a*) *Stannic Acid*, H_2SnO_3, is obtained when calcium carbonate is treated with an excess of stannic chloride. *Sodium Stannate*, Na_2SnO_3, is largely used as a preparing salt in calico-printing.

(*b*) *Stannous Sulphide*, SnS, is a brown substance, while *Stannic Sulphide*, SnS_2, is a yellow one. These precipitates are produced in the regular course of analysis when the solution contains the corresponding salts of tin. They are soluble in yellow ammonium sulphide.

141. Tests for Tin. — 1. Metallic tin is recognized by its lustre and by the emission of a crackling sound when bent or bitten.

2. Any solid containing tin, or metallic tin itself, when heated on charcoal in the oxidizing flame, gives a coating

around the assay which is pale yellow while hot and white when cold.

3. A solid may be tested by dissolving in hydrochloric acid and then adding a solution of mercuric chloride. At first a white precipitate, Hg_2Cl_2, is obtained. This soon turns black, metallic mercury being set free. See Art. 130, 3.

BISMUTH.

142. Occurrence and Preparation. — Bismuth usually occurs native, but it is always contaminated with a small percentage of other metals. Its chief ores are bismuth ochre, Bi_2O_3, and bismuthite, Bi_2S_3.

Exp. 89. Make a pellet of any bismuth compound with sodium carbonate and a drop of water. Heat this pellet on charcoal in the reducing flame, and test the bead obtained, as usual. Then heat the bead in the oxidizing flame, and note the coating, Bi_2O_3, which is formed around the assay.

Bismuth can be partially obtained by heating its ores; but the extraction is made complete by first roasting the ore, after which it is fused with iron slag and charcoal. The crude bismuth thus obtained is purified by fusing it at the lowest possible temperature on an inclined plane; the molten metal runs slowly down the plane, while the impurities remain behind.

143. Properties and Compounds of Bismuth. — Bismuth is a hard, brittle metal of a grayish white color, with a distinct tinge of red. It oxidizes slowly in the atmosphere. It is not employed in a pure state, but is chiefly used in making alloys and in making pharmaceutical preparations. Bismuth alloys expand while cooling. The fusible metals

used in stereotyping and in electrotyping are alloys of bismuth with lead, tin, and cadmium.

Bismuth forms two series of salts similar to antimony. In one class bismuth acts as a triad; in the other, BiO appears, acting as a monad. The salts of the latter are called bismuthyl salts. $Bi(NO_3)_3$ and $BiONO_3$ are examples.

Nitric acid is a good solvent for bismuth when a working compound is desired. But the solution in water must be acid, as water changes bismuth nitrate into bismuthyl nitrate, an insoluble compound.

Some compounds of bismuth follow : —

(a) Of the *Bismuth Oxides*, Bi_2O_3 is the principal one. It is used as a pigment.

(b) *Bismuth Nitrate*, $Bi(NO_3)_3 + 3 H_2O$, is obtained by the action of the metal on nitric acid. *Bismuthyl Nitrate*, $BiONO_3H_2O$, is the so-called Subnitrate of Bismuth of the pharmacopœia. It is obtained by adding water to the nitrate. It is used in medicine as a remedy for cholera and dysentery. It is also used as a cosmetic under various names, as Blanc d'Espagne and Blanc de Fard. It is further used in glazing porcelain, to which it imparts an iridescent surface.

(c) *Bismuth Trisulphide*, Bi_2S_3, is the black precipitate obtained in analysis. It is soluble in hot nitric acid.

144. Tests for Bismuth.—1. Any bismuth compound when heated with sodium carbonate on charcoal gives a metallic bead. If the bead be heated in the oxidizing flame, a coating is obtained around the assay of bismuth trioxide, Bi_2O_3. This coating is orange-yellow while hot, lemon-yellow when cold, and the edges of the coating are bluish white.
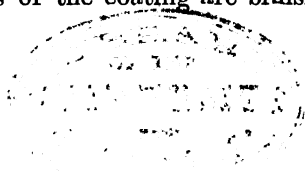
2. An unknown solution may be tested as follows : —

(*a*) Add water to the solution. A white precipitate of a bismuthyl salt is obtained, provided the solution be not too acid.

(*b*) Ammonia gives a white precipitate, $Bi(OH)_3$.

(*c*) $K_2Cr_2O_7$ gives a yellow precipitate, $(BiO)_2Cr_2O_7$ which is insoluble in KOH — a distinction from lead.

(*d*) H_2S gives a black precipitate, Bi_2S_3, soluble in hot nitric acid.

COPPER.

145. Occurrence and Preparation. — Copper occurs native in large quantities. The most plentiful deposits are found in Upper Michigan, where it is found in sheets or veins intersecting red sandstone and trap rocks; but the largest deposits are found as granular masses mixed through a rocky matrix. Masses of pure copper weighing tons have been found.

The argentiferous ores of the Rocky Mountains also furnish a large amount of copper. Many other localities afford copper, both free and combined.

The commercial preparation of copper is a simple process when applied to the native copper deposits. The pure copper is simply freed from all impurities by smelting.

Exp. 90. Place a bright steel nail in a solution of copper sulphate, $CuSO_4$. Note the coating of copper.

The reduction of copper from its solutions has many familiar illustrations. The plates of gravity-batteries soon become covered with a deposit of metallic copper. In electrotyping, copper is deposited upon a wax mould of the type; and many metals, when placed in a copper solution, receive a coating of copper.

146. Properties and Compounds of Copper. — Copper is a tough, malleable metal which soon tarnishes in moist air containing carbon dioxide. It is a good conductor of electricity, and enormous quantities of copper are used in making wire for electrical purposes. Sheet copper is largely used in making household utensils and in sheathing ships for ocean navigation.

Copper was used by prehistoric man for making all kinds of weapons and utensils which his rude ingenuity could devise.

There are two series of copper salts and no copper acids. Copper sulphate affords a good working solution in the laboratory. Copper sulphate, or blue vitriol, as it is often called, is the principal compound of copper to be found in the market. The formula of the crystals is

$$CuSO_4 + 5 H_2O.$$
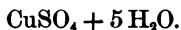
147. Tests for Copper. — 1. A solid is to be dissolved in nitric acid and the solution tested by 2.

2. A solution of copper is tested by adding ammonia. When the amount of the ammonia is short of an excess, a white precipitate is formed; but as soon as an excess of ammonia is added, the precipitate dissolves, and a splendid blue solution is formed.

3. H_2S gives a black precipitate, which may be dissolved in nitric acid and tested by 2.

CADMIUM.

148. Occurrence and Preparation. — Cadmium is a somewhat rare metal occurring associated with zinc. In the zinc furnaces cadmium is oxidized to CdO, a vapor which is condensed and afterward reduced by heating in closed

tubes with charcoal. The uses of the free metal are very limited.

Cadmium is a tin-white metal which slowly oxidizes in the air, which imparts to the metal a yellowish cast. When strongly heated in the air, it burns, forming the oxide, CdO.

Cadmium iodide, CdI_2, is used in photography. The sulphide, CdS, is obtained in analysis.

149. Tests for Cadmium.— 1. A solid containing cadmium when heated on charcoal in the oxidizing flame yields brownish yellow fumes of CdO. The coating around the assay is of the same color.

2. A solution containing cadmium gives the yellow precipitate, CdS, with H_2S.

150. Separation and Identification of the Second Group Metals. — After removing the first group metals with hydrochloric acid, hydrogen sulphide, H_2S, is passed for a long time through the acid filtrate. If any or all of the second group metals are present in the filtrate, they are precipitated as sulphides. First these sulphides are filtered out, and then they must be washed with much water, as they lie on the filter-paper. Then make a hole in the point of the paper, and by means of a stream of water from a blow-bottle, wash the precipitate through into an evaporating-dish. Now add yellow ammonium sulphide and digest for some time. The sulphides of arsenic, antimony, and tin will dissolve, while the sulphides of bismuth, copper, and cadmium are unaltered. Filter the contents of the evaporating-dish. Treat the filtrate by I.; treat the residue on the filter-paper by II.

I.

ARSENIC, ANTIMONY, AND TIN.

To the filtrate add hydrochloric acid. The sulphides of arsenic, antimony, and tin are re-precipitated. Filter and wash the precipitate, and then wash it through into an evaporating-dish. Add *concentrated* hydrochloric acid and boil as long as the odor of hydrogen sulphide can be detected. The sulphide of arsenic remains undissolved, while those of tin and antimony are dissolved. Filter the contents of the evaporating-dish, and test the residue on the filter-paper for arsenic by Art. 135, 1 and 3.

To the filtrate add a few pieces of metallic zinc. Antimony and tin are both reduced to the metallic state. Pour off the solution, and wash the two metals in water by decantation. Add hydrochloric acid to the metals. Only the tin is dissolved. Filter, and test the filtrate for tin by Art. 141, 3.

Metallic antimony remains on the filter-paper. Test by Art. 138, 1. Also dissolve in hot nitro-hydrochloric acid, and test by Art. 138, 2.

II.

BISMUTH, COPPER, AND CADMIUM.

Add hot nitric acid to the sulphides of these metals as they are lying on the filter-paper. The sulphides all dissolve;[1] save the solution as it runs through, and evaporate

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[1] If a black residue remains after treating with nitric acid, it is probably mercury in the mercuric condition. Therefore dissolve this black residue in nitro-hydrochloric acid, expel the excess of acid, and add $SnCl_2$. See Art. 130, 3.

it to dryness to expel the excess of acid. Dissolve the residue in water and then add an excess of ammonia.[1]

1. The bismuth is precipitated as bismuth hydroxide, $Bi(OH)_3$; copper and cadmium remain in solution. Filter out the $Bi(OH)_3$, and save the filtrate to test by 2; dissolve the $Bi(OH)_3$ in a little hydrochloric acid and expel any excess of acid; a little water will now give a white precipitate of bismuthyl chloride, BiOCl. This is sufficient to identify the bismuth.

2. When ammonia was added, if copper salts were present, the solution turned blue. No further identification of copper is necessary. In order to determine if cadmium be present, add to the blue solution a solution of potassium cyanide, KCN, until the blue color is destroyed. Now pass hydrogen sulphide through the solution. If cadmium be present, it will be precipitated as the yellow sulphide, CdS. Test this sulphide by Art. 149, 1.

GOLD AND PLATINUM.

151. Gold. — Gold always occurs native. It is widely distributed in the older sedimentary and igneous rocks. Rivers running through these rocks wash down fine particles of gold and sand. From these sands the miner separates the gold by washing in shallow pans or cradles. Lumps or nuggets of gold have been found, of great value, especially in California and in Australia.

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[1] If lead was found in the first group, it will almost be sure to appear in the solution containing bismuth, copper, and cadmium. Therefore in such a case, before adding ammonia, try a small portion of the solution with sulphuric acid. If a precipitate appears, add the acid to the whole solution, and thus precipitate the lead as $PbSO_4$. Filter out the precipitate, and then to the filtrate add an excess of ammonia, etc.

On the Pacific coast of the United States man has imitated nature by directing powerful streams of water against the sides of hills from which some of the rivers obtain their supply of gold-dust. The detritus washed down is conveyed through sluices, in the bottom of which are placed pockets containing mercury to catch the gold as it comes along. The gold is separated from the mercury by heat.

Gold occurs also in quartz rock. In such cases the rock is crushed to dust, and the gold is recovered by amalgamation.

Gold has been known and prized as a precious metal from the earliest times. It is usually necessary to alloy the gold with a harder metal before it is made into coins and jewelry. Silver and copper are employed to give the requisite amount of hardness to gold employed for these purposes.

152. Platinum. — Platinum is a silver-white metal of great use to the chemist, who uses it in the form of wire, foil, crucibles, and evaporating-dishes.

Platinum is infusible at temperatures usually employed in the laboratory, but it can be fused in the oxyhydrogen flame. It does not tarnish in the air, and is insoluble in all acids except nitro-hydrochloric acid. It is also insoluble in the alkalies.

Platinum, like gold, always occurs native. It is obtained free from other metals of a kindred nature which always accompany it, in the wet way. The platinum-bearing compounds are dissolved in aqua regia, when platinum and the accompanying metals are changed into chlorides. Ammonium chloride is next added to the solution, when the platinum is precipitated as a double chloride of platinum and ammonium, $(NH_4)_2PtCl_6$. This precipitate, when

heated, yields spongy platinum. Finally, the platinum is brought into a coherent condition by heating it in lime crucibles in the oxyhydrogen flame.

EXERCISES.

(*For Review or Advanced Course.*)

1. Compute the atomic heat for each of the second group metals.

2. Write a list of the salts formed by tin, copper, bismuth, and cadmium.

3. Determine by experiment if each of the second group metals is reduced from a solution of its salts by metallic zinc.

4. Write the reaction for each of the following metals with nitric acid : copper, bismuth, and cadmium.

5. Select some soluble salt for each of the second group metals, and then write the reaction between the salt selected and hydrogen sulphide.

CHAPTER XII.

THE THIRD GROUP METALS.

DATA FOR COMPUTATIONS. — IRON: Symbol, Fe'', Fe_2^{vi}; Atomic Weight, 56; Specific Heat, 0.1140; Melting-point, a white heat; Specific Gravity, 7.86. — CHROMIUM: Symbol, Cr'''; Atomic Weight, 52; Specific Heat, 0.09975; Melting-point, higher than the temperature of the oxyhydrogen flame; Specific Gravity, 6.50. — ALUMINUM: Symbol, Al'''; Atomic Weight, 27; Specific Heat, 0.2140; Melting-point, 700°; Specific Gravity, 2.60. — NICKEL: Symbol, Ni''; Atomic Weight, 58; Specific Heat, 0.1080; Melting-point, nearly a white heat; Specific Gravity, 8.90. — COBALT: Symbol, Co''; Atomic Weight, 59; Specific Heat, 0.10674; Melting-point, a white heat; Specific Gravity, 8.5 to 8.7. — MANGANESE: Symbol, Mn''; Atomic Weight, 55; Specific Heat, 0.1217; Melting-point, a white heat; Specific Gravity, 8.03. — ZINC: Symbol, Zn''; Atomic Weight, 65; Specific Heat, 0.0955; Melting-point, 423°; Specific Gravity, 7.15.

153. The Third Group Metals are precipitated from the filtrate obtained when the second group metals are filtered out. This filtrate, as previously mentioned, needs a little preliminary treatment before the reagents are applied. Iron must always be present in the ferric condition. The hydrogen sulphide employed to throw down the second group metals has reduced any iron compounds to the ferrous condition. Moreover, it has reduced chromium, if present as an acid, to chromium as a base, which leaves the chromium in a proper condition for the application of the necessary reagents. In deference to any iron that may be present it is necessary to boil the filtrate until all hydrogen sulphide be removed, after which nitric acid is added,

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and the solution is boiled again for a short time. The nitric acid added oxidizes iron, if present, to the ferric state, and the solution is now ready for the application of the needed reagents.

Accordingly ammonia and ammonium chloride are immediately added, and thus are iron, chromium, and aluminum precipitated as the hydroxides, $Fe_2(OH)_6$, $Cr_2(OH)_6$, and $Al_2(OH)_6$. These precipitates are now removed by filtration and to the filtrate, ammonium sulphide, $(NH_4)_2S$, is added. Thus are obtained as precipitates the sulphides, NiS, CoS, MnS, and ZnS. This completes the precipitation of the third group metals.

IRON.

154. Occurrence and Preparation. — Metallic iron occurs only in insignificant quantities. Meteorites usually contain metallic iron together with other metals. But the compounds of iron are distributed almost everywhere. The color of vegetation is due to iron compounds, and nearly every soil contains some form of combined iron. Its ores are widely distributed, but the localities are somewhat restricted in extent. Iron pyrites, FeS_2, or fool's gold, is a well-known mineral on account of its yellow lustre resembling gold.

Of the ores employed in the United States for preparing commercial iron, the most important is hæmatite, Fe_2O_3. This ore assumes a variety of forms. The amorphous form resembles iron rust, while the micaceous ore occurs in glittering scales. Bog ore, $Fe_2O_3 + Fe_2(OH)_6$, also called brown hæmatite, is the ore chiefly employed in Germany and France. Argillaceous ore, or clay iron-stone, is employed in England. Magnetite or lodestone, Fe_3O_4, is

interesting on account of its constituting the natural magnet.

The reduction of iron from its ores is one of the most important industries of the age, and the furnaces and the machinery required are expensive. The form of the modern blast-furnace is shown in Fig. 29. It is from fifty to ninety feet high, and from fourteen to twenty feet broad in its widest part. It is constructed of masonry, lined with fire-brick, and enclosed down to the point A in riveted iron boiler-plates. Before the furnace goes into blast, the masonry does not extend below A, but the stack is supported on strong iron pillars resting on a solid foundation. These pillars are not shown in the cut. The hearth, H, consists of fire-clay, and

FIG. 29.

it is here that the molten iron collects. There are two openings in this hearth: the lower one for drawing off the cast iron, and the upper one for removing the glassy slag obtained during the reduction of the ore. The top of the stack D is funnel-shaped, and is closed by an inverted cone, E, which can be raised or lowered while charging the furnace.
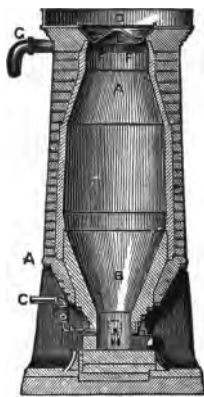
When the furnace is about to go into blast, the spaces H and B are filled with cord-wood, after which the whole portion below A is enclosed by masonry. A number of blow-pipes, or "tuyeres," are built into the masonry. Through these, powerful blasts of air are maintained when the furnace is in operation.

In starting the furnace, the wood is first ignited and the blast is turned on. Then stone-coal is introduced at the

top of the stack.   When the stack has become thoroughly heated, finely crushed ore, stone-coal, and limestone are regularly added at the top of the stack.   Barring accidents, a furnace runs night and day, shutting down but once or twice a year to repair the stack.

The chemical changes which occur in the stack are not well understood, but the products obtained are cast iron, a glassy slag, carbon dioxide, carbon monoxide, hydrogen, cyanogen, graphite, and perhaps certain hydrocarbons.   These gases, some of which are inflammable, are not wasted, but are led through the pipe G to boilers which furnish steam to the engines that run the machinery employed.

The iron obtained from the blast-furnace is not pure iron.   It is called *cast iron*, and contains carbon, silicon, traces of arsenic, sulphur, and phosphorus, and small quantities of various metals.

From this cast iron, *wrought iron* is obtained by the processes termed " refining " and " puddling."   In these operations the impurities are burned out and the metal is hammered into coherence, after which it is rolled into bars and sent to market.
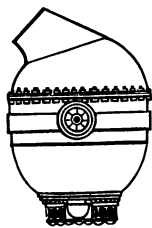
FIG. 30.

Steel is now obtained by the Bessemer process from cast iron.   The molten cast iron is run into an egg-shaped vessel, called a " converter " (Fig. 30), and a blast of air is driven up through the molten metal.   The impurities are thus burned out, leaving nearly pure iron.   Steel stands about midway in its content of carbon and silicon between cast and wrought iron.   In order to furnish the proper amounts of these two substances, a pure variety of cast iron, called " spiegel iron," is now added to the pure iron, thus converting the whole into steel.

155. Properties and Compounds of Iron. — Iron is a nearly silver-white metal that rusts quickly when exposed to damp air, thus receiving a coating of ferric oxide and ferric hydroxide. It is a tenacious metal which possesses the property of softening before it melts, thus allowing different pieces to be welded.

The uses of iron are so many and so important that this age has been well termed the *iron age*.

Iron forms two series of salts, — the ferrous and the ferric. These salts are exemplified by the two chlorides, ferrous chloride, $FeCl_2$, and ferric chloride, Fe_2Cl_6. It will be noticed that in the ferrous compounds iron is bivalent, while in the ferric state two atoms are hexavalent. As in the mercurous compounds, the ferric salts are written with an even number of atoms.

Iron dissolves in almost any of the acids, and any of the salts make good working solutions. Some of the more important compounds follow : —

(a) *Ferric Hydroxide*, $Fe_2(OH)_6$, is obtained by adding ammonia to almost any ferric salt. It is the precipitate obtained in analysis.

(b) *Ferric Chloride*, Fe_2Cl_6, is obtained when iron wire is dissolved in hydrochloric acid, after which the solution is thoroughly saturated with chlorine gas. It is used in medicine, and in the laboratory it is an important reagent.

(c) *Ferrous Sulphate*, $FeSO_4 + 7 H_2O$, is often called copperas and green vitriol. It may be obtained by dissolving iron or ferrous sulphide in sulphuric acid. The commercial article is often prepared by roasting iron pyrites at a moderate heat. It is used as a disinfectant, as a reagent, and in preparing fuming sulphuric acid. It is also used in dyeing.

(d) *Ferrous Sulphide*, FeS, is made by stirring molten

sulphur with a white-hot wrought-iron rod. It is used in the laboratory as a source of hydrogen sulphide.

(e) *Potassium Ferrocyanide*, $K_4Fe(CN)_6$, is obtained by heating scrap iron in closed iron retorts with potash and animal matter, such as hoofs, horns, etc.

This compound serves as the starting-point in the manufacture of all of the cyanogen compounds. It is used in the manufacture of Prussian blue, $Fe_7(CN)_{18}$. This pigment is obtained when ferric chloride is added to potassium ferrocyanide. In the laboratory, potassium ferrocyanide is used as a reagent for the detection of iron. The ferricyanide is obtained by oxidizing the ferrocyanide with chlorine. Its formula is $K_3Fe(CN)_6$.

156. Tests for Iron. — 1. Solids are first brought into solution by using water as a solvent. If water will not dissolve the solid, an acid is used. The solution is then tested by 2.

2. For testing a solution for iron, the reagents potassium sulphocyanide, KCNS, potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$, are used. Ferrous and ferric salts act differently, as shown by the following table : —

REAGENT.	FERRIC SALT.	FERROUS SALT.
KCNS	Red sol. $Fe_2(CNS)_6$	No change.
$K_4Fe(CN)_6$	Deep blue prec. $Fe_4[Fe(CN)_6]_3$	Pale blue prec. $K_2Fe, Fe(CN)_6$
$K_3Fe(CN)_6$	No prec. Reddish brown sol.	Deep blue prec. $Fe_3[Fe(CN)_6]_2$

3. Ferrocyanic, ferricyanic, and sulphocyanic acids may be detected by employing as reagents ferric chloride, Fe_2Cl_6, and ferrous sulphate, $FeSO_4$, by means of the table given in 2.

CHROMIUM.

157. Occurrence and Preparation. — Chromium is a rare metal not employed in the arts. Its chief ores are crocoisite, or chrome yellow, $PbCrO_4$, and chrome iron-stone, $Cr_2O_3(FeO)$. Small quantities of the metal are obtained by mixing its oxide with sugar, after which the mixture is strongly heated in lime crucibles.

158. Properties and Compounds. — Chromium imparts a superior hardness to steel. Its compounds are numerous and important. It acts as a base, and is also an acid-forming element. Potassium bichromate and chrome alum answer well for working purposes in the laboratory. These compounds and a few others are noticed.

(*a*) *Chromic Oxide*, Cr_2O_3, is obtained by fusing potassium bichromate with sulphur or with ammonium chloride, after which the fused mass is treated with water. It is used in coloring glass and enamel green. This oxide may be regarded as the anhydride of the hypothetical chromic acid, H_2CrO_4. Chromic hydroxide, $Cr_2(OH)_6$, is obtained when ammonia is added to a solution containing *chromium as a base.*

(*b*) *Guignet's Green*, or chrome green, $Cr_2O(OH)_4$, is used as a pigment. It is obtained by fusing potassium bichromate and crystallized boric acid mixed in proportions corresponding to their molecular weights.

(*c*) *Chrome Alum*, or potassium chromium sulphate, $K_2Cr_2(SO_4)_4 + 24\,H_2O$, is used in dyeing, tanning, and in calico-printing. It is obtained as a by-product in the manufacture of alizarine.

(*d*) *Potassium Bichromate*, $K_2Cr_2O_7$, is obtained from

chrome iron ore.   The ore is first roasted to oxidize it, and
then it is fused with lime and potassium carbonate; then
the fused mass is leached with as little water as possible,
and the filtrate is treated with sulphuric acid.   This salt
is extensively used in batteries, in dyeing, in preparing the
pigment, chrome yellow, $PbCrO_4$, and other compounds,
and as a reagent.

159. Tests for Chromium. — 1. A solid is fused on char-
coal with potassium nitrate and sodium carbonate in order
to oxidize any chromium present to a chromate.   Now dis-
solve the yellow mass obtained in water, and add acetic
acid to an acid reaction.   Finally, add lead acetate, when a
yellow precipitate, $PbCrO_4$, will be obtained.

2. A chromate or a bichromate in solution gives with —

Hydrogen sulphide, H_2S, a green solution ;

Lead acetate, $Pb(C_2H_3O_2)_2$, a yellow precipitate, $PbCrO_4$;

Silver nitrate, $AgNO_3$, a brownish red precipitate,
$AgCrO_4$.

ALUMINUM.

160. Occurrence and Preparation. — Although metallic
aluminum never occurs free, in compounds it occurs in
enormous quantities.   It ranks next to oxygen and silicon
in its abundance.   It is the basis of clayey soils, and it
occurs as feldspar, $K_2Al_2Si_6O_{16}$, in many different kinds of
rocks.   Kaolin, or porcelain clay and china clay, is simply
weathered feldspar.

Aluminum trioxide, Al_2O_3, is well known as corundum or
emery.   Crystallized forms of this substance are known as
the jewels sapphire, ruby, oriental emerald, oriental topaz,
and oriental amethyst.   Other gems also have aluminum
as a base: thus, turquoise is a phosphate of aluminum

colored with copper; topaz and beryl are silicates of aluminum.

Aluminum can only be reduced from its ores by expensive processes. Of late the metal has been prepared by reducing the trioxide mixed with carbon in lime crucibles by means of electricity.

161. Properties and Compounds. — Aluminum is a white, malleable metal that does not tarnish under ordinary circumstances. Its physical properties fit it for many uses that the great cost of its production alone forbids. It is chiefly employed at present in making philosophical instruments. Aluminum bronze is now being much used for making ornamental household fixtures.

Any one of the alums affords a good working solution. Several compounds that have not been noted follow : —

(a) *Aluminum Hydroxide*, $Al_2(OH)_6$, is obtained when ammonia is added to any soluble aluminum salt. It is the precipitate obtained in analysis.

(b) *Aluminum Sulphate*, $Al_2(SO_4)_3$, is obtained by acting on roasted kaolin with sulphuric acid. This is used in immense quantities as a mordant and for weighting paper.

(c) The alums are an interesting class of compounds. The formula for potassium alum will serve as a type for all the others, $K_2Al_2(SO_4)_4 + 24\,H_2O$. In place of the potassium, other metals may be substituted; thus we have silver alum, ammonium alum, chromium alum, etc.

(d) *Sodium Aluminate* is prepared by fusing bauxite, $Al_2Fe_2O_8H_4$, with sodium sulphate and carbon. It is used as a mordant in dyeing and in calico-printing, for preparing colored lakes and for sizing paper.

162. Tests for Aluminum. — 1. A solution is tested by 2. A solid is first fused on charcoal with sodium carbonate, the fused mass is dissolved in hydrochloric acid, and the solution tested by 2.

2. A solution is tested as follows : —

(*a*) An excess of ammonia and ammonium chloride gives a white, gelatinous precipitate, $Al_2(OH)_6$.

(*b*) A solution of sodium carbonate gives the same precipitate.

(*c*) Disodium phosphate gives a white precipitate, $Al_2(PO_4)_2$, soluble in potassium hydroxide, insoluble in acetic acid.

NICKEL.

163. Occurrence and Preparation. — Nickel never occurs free. Its ores occur in connection with the cobalt ores. The most important ore is kupfer-nickel, $NiAs$. Metallic nickel is obtained mostly in the wet way. The ore is first roasted, and then dissolved in hydrochloric acid. This solution usually contains the chlorides of other metals as well as nickel chloride. These foreign metals are precipitated by the addition of proper reagents, leaving the nickel in solution, from which it is precipitated by adding sodium hydroxide. The nickel hydroxide, $Ni(OH)_2$, thus obtained is reduced by the action of charcoal at high temperatures.

164. Properties and Compounds of Nickel. — Nickel is a white, hard metal, susceptible of a high polish and scarcely tarnishing in the air. It is accordingly used for coinage and for nickel-plating other metals, especially iron. German silver is an alloy of copper, 5 parts; nickel, 2 parts; and zinc, 2 parts. Nickel resembles iron in that it can be welded and can be attracted by the magnet.

Nickel is soluble in dilute nitric acid, yielding nickel nitrate, $Ni(NO_3)_2$, which affords a good working solution. The chloride and sulphate are also to be had by using the proper acids. The salts of nickel are used but little. The sulphide, NiS, is the black precipitate obtained in analysis. It is soluble in nitro-hydrochloric acid.

165. Tests for Nickel. — A solid supposed to contain nickel is brought into solution by means of nitro-hydrochloric acid, if water will not dissolve it, and tested thus : —

(*a*) Ammonia, when added to a solution short of an excess, produces an apple-green precipitate, $Ni(OH)_2$. An excess of ammonia gives a blue solution. To this blue solution add potassium hydroxide, when the apple-green hydroxide again appears.

(*b*) Potassium hydroxide added directly to a nickel solution gives the same apple-green precipitate.

2. Any nickel compound in a borax bead in the oxidizing flame colors the bead brownish red while hot, yellow when cold. In the reducing flame the bead becomes gray, metallic nickel being reduced. Cobalt interferes with this test.

COBALT.

166. Occurrence and Preparation. — Cobalt does not occur free, neither is the metal used in the arts. Speiss cobalt, $Co(Ni,Fe)As_2$, Skutterudite, $CoAs_3$, and cobalt glance, $CoFeAs_2S_2$, are the more important ores.

Metallic cobalt is obtained as a gray metallic powder by heating the oxide or chloride in an atmosphere of hydrogen.

The compounds of cobalt are used in the arts, and they are prepared directly from a cobalt ore, usually speiss cobalt.

167. Properties and Compounds. — Cobalt resembles iron in color and in being attracted by the magnet. The compounds of cobalt are useful as furnishing valuable pigments. Some compounds follow : —

(*a*) *Cobalt Oxide*, CoO, is an article of commerce. It is used in coloring glass blue and in preparing the cobalt pigments. It may be dissolved in acids, forming salts of the acids used. This oxide is prepared from speiss cobalt. The ore is first roasted, then dissolved in hydrochloric acid, and then the accompanying metals are precipitated by adding successively chlorine, limestone, and hydrogen sulphide. The oxide is now precipitated by the addition of bleaching-powder.

(*b*) *Cobaltous Chloride*, $CoCl_2$, is used as a sympathetic ink. Its action depends on the fact that when moist the salt is a light pink, but when dry it is violet. Thus the writing becomes visible when the paper is warmed.

(*c*) *Cobaltous Nitrate*, $Co(NO_3)_2$, is used in the laboratory as a reagent. It can be made by dissolving the metal or the carbonate of the metal in nitric acid.

(*d*) *Cobaltous Sulphide*, CoS, is the precipitate obtained in analysis. It is soluble in nitro-hydrochloric acid.

(*e*) Smalt is a silicate of cobalt used as a pigment.

168. Tests for Cobalt. — 1. Any cobalt compound colors the borax bead blue. If an excess of cobalt be present, the bead may be almost black. When powdered, the dust from this bead is blue in all cases.

MANGANESE.

169. Occurrence and Preparation. — Manganese never occurs free nor is it used in the arts. Its chief ore is pyro-

lusite, MnO_2. It is obtained in the metallic state by fusing one of its oxides mixed with charcoal at a white heat in a closed crucible lined with graphite.

170. Properties and Compounds. — Manganese is a reddish white metal, oxidizing so readily that it is necessary to preserve it under naphtha or coal oil. Some of the manganese compounds follow: —

(*a*) *Manganese Dioxide*, MnO_2, is the most important of the oxides of manganese. It is used with hydrochloric acid in large quantities for generating chlorine gas in the manufacture of bleaching-powder. Its use in the laboratory has already been exemplified.

(*b*) *Potassium Permanganate*, $K_2Mn_2O_8$, is used in the laboratory, and an impure form of sodium permanganate is used as a disinfecting fluid under the name of Condy's Disinfecting Liquid. These salts may be regarded as originating from the acid, $HMnO_4$, or permanganic acid. Manganic acid, H_2MnO_4, has not been isolated, but the manganates are known.

(*c*) *Manganese Sulphide*, MnS, is the flesh-colored precipitate obtained in analysis. It is soluble in cold dilute hydrochloric acid.

171. Tests for Manganese. — 1. Manganese compounds in the oxidizing flame give the borax bead a violet color while hot, amethyst-red when cold. In the reducing flame the bead becomes colorless.

2. A solid may be fused on platinum or on porcelain with sodium carbonate and potassium nitrate to a bright green mass, a manganate. Dissolve this mass in nitric acid, and a permanganate is obtained in a red solution.

ZINC.

172. Occurrence and Preparation. — Zinc does not occur free in significant quantities. Smithsonite, $ZnCO_3$, is one of the principal ores. Franklinite, $(Zn,Fe)O + Fe_2O_3$; zinc blende, ZnS; Willemite, Zn_2SiO_4, and a reddish oxide owing its color to an oxide of manganese, are the principal ores employed in the United States.

The ores are first roasted and then ground fine; then they are mixed with half their weight of coal-dust. Now the mixture is placed in clay retorts and heated until the zinc issues in the form of a vapor, which is condensed in iron condensers. Commercial zinc as thus prepared is seldom pure, as it contains small quantities of other metals.

173. Properties and Compounds. — Zinc is a malleable, ductile, bluish-white metal which finds many uses. Sheet zinc and galvanized iron, which is sheet iron coated with zinc, are familiar to all. Zinc alloyed with copper forms the useful alloy, brass. For batteries and in the laboratory, zinc is used extensively.

Zinc dissolves in most of the acids to form salts that are applicable for working purposes. When taken internally the salts of zinc are poisonous.

(*a*) *Zinc Chloride*, $ZnCl_2$, is obtained when the metal is dissolved in hydrochloric acid. This salt is used as a caustic in surgery; and in organic chemistry it is used for removing the elements of water from many substances. It is used in weighting cotton goods, and in tin-shops as a soldering-fluid.

(*b*) *Zinc White*, ZnO, is used as a paint.

(*c*) *Zinc Sulphate*, or white vitriol, $ZnSO_4 + 7 H_2O$, is used in medicine and in dyeing.

(*d*) *Zinc Sulphide*, ZnS, is the white precipitate obtained in analysis.

174. Tests for Zinc. — 1. Solids, when heated on charcoal in the oxidizing flame, give a coating around the assay, yellow while hot, and white when cold.   If now the mass and the coating be moistened with cobaltous nitrate and heated again, the pigment, Rinnman's green, is obtained.

2. A solution gives a white precipitate, ZnS, when ammonia and ammonium sulphide are added.

SEPARATION OF THE THIRD GROUP METALS.

175. Precipitate the iron, chromium, and aluminum as explained in Art. 153.   Filter out the precipitate obtained, wash with water, and then proceed by I.

Precipitate the remaining metals of this group by adding ammonium sulphide.   Warm the solution until the sulphides settle, then filter, wash the precipitate, and proceed by II.

I.

IRON, CHROMIUM, AND ALUMINUM.

1. Pierce the point of the filter-paper and wash the precipitate through into an evaporating-dish.   Take a small portion of this precipitate and dissolve it in nitric acid with heat.   Divide the solution thus obtained in two parts and test directly for iron.   Potassium sulphocyanide gives a red solution ; potassium ferrocyanide gives a deep blue precipitate.   (See Art. 156.)   The presence of chromium and aluminum will not interfere with the tests for iron.

If iron be found, test a portion of the original solution to determine whether the iron in it is in the ferrous or ferric condition.

2. For chromium, take a second portion of the hydroxides in the evaporating-dish, fuse it on charcoal with sodium carbonate, etc., as in Art. 159, 1.

3. To the remainder of the precipitate in the evaporating-dish add potassium hydroxide and boil. The aluminum will dissolve. Filter, and barely acidify the filtrate with hydrochloric acid; and then add ammonia in excess. A white precipitate, $Al_2(OH)_6$, identifies aluminum.

II.

NICKEL, COBALT, MANGANESE, AND ZINC.

1. Wash the sulphides of these metals through into a test-tube and add cold, dilute hydrochloric acid; shake frequently. The sulphides of nickel and cobalt do not dissolve, but manganese and zinc are brought into solution. Filter, and treat any residue for nickel and cobalt by 3. Treat the filtrate for manganese and zinc by 2.

2. Boil this filtrate to expel hydrogen sulphide, then add a decided excess of potassium hydroxide. Allow the tube to stand, and shake frequently. Any manganese will be precipitated as $Mn(OH)_2$. Filter, and test the precipitate by Art. 171. Test the filtrate for zinc by acidifying with acetic acid and adding ammonium sulphide. Any zinc will give the white precipitate, ZnS. Farther test this precipitate by Art. 174, 1.

3. This residue contains some sulphur obtained from the sulphides that dissolved. Test a portion of the residue by the borax bead. A blue bead identifies cobalt.

If both nickel and cobalt are present, it is somewhat difficult to obtain the tests for nickel, but it may be accomplished thus: dissolve the remainder of their sulphides in nitro-hydrochloric acid, and add to the solution an excess of potassium hydroxide. A precipitate may be $Co(OH)_2$ and $Ni(OH)_2$. Filter out this precipitate and dissolve it in acetic acid. To this solution add potassium nitrite, KNO_2. Allow the tube to stand twenty-four hours. Any precipitate will be potassium cobaltic nitrite; this leaves the nickel in solution. Precipitate it by adding potassium hydroxide, and thus obtain the apple-green hydroxide, $Ni(OH)_2$.

EXERCISES.

(For Review or Advanced Course.)

1. Compute the atomic heat for each of the third group metals.

2. Determine by trial if any of the third group metals can be reduced from compounds to the metallic state by means of the blow-pipe, charcoal, and sodium carbonate.

3. Write the equations for the separation of the third group metals.

4. Obtain a bit of alum from the drug store, and test it for aluminum.

5. Dissolve a bit of iron in hydrochloric acid. Write the reaction. Do you obtain ferrous or ferric chloride ? Test by Art. 156.

CHAPTER XIII.

THE FOURTH GROUP METALS.

DATA FOR COMPUTATIONS. — BARIUM: Symbol, Ba'; Atomic Weight, 137; Specific Heat, ——; Melting-point, higher than cast iron; Specific Gravity, 3.75. — STRONTIUM: Symbol, Sr''; Atomic Weight, 87.2; Melting-point, a red heat; Specific Heat, ——; Specific Gravity, 2.54. — CALCIUM: Symbol, Ca''; Atomic Weight, 40; Specific Heat, 0.1804; Melting-point, a red heat; Specific Gravity, 1.57. — MAGNESIUM: Symbol, Mg''; Atomic Weight, 24; Specific Heat, 0.2450; Melting-point, 750°; Specific Gravity, 1.74.

176. The fourth group metals, often called the "Metals of the Alkaline Earths," are obtained from the filtrate from which the third group has been removed, as explained in Art. 153. This filtrate needs preliminary treatment. It is loaded down with reagents after passing through the operations required in the preceding groups. It is best, therefore, to evaporate it strictly to dryness, and even to ignite the residue gently in order to expel these reagents as far as possible. Then dissolve the residue in water, when it will be ready for the fourth group reagents.

Barium, strontium, and calcium are precipitated as the carbonates, $BaCO_3$, $SrCO_3$, and $CaCO_3$, by the addition of ammonia, ammonium chloride, and ammonium carbonate. These metals are then filtered out, and magnesium is obtained directly from a portion of the filtrate by adding disodium phosphate, which gives the double phosphate, $MgNH_4PO_4$.

It is evident that the remaining portion of the filtrate

contains, beside the magnesium that may be present, the fifth group metals. Now since magnesium does not interfere with the flame-tests for these metals, this portion of the filtrate is retained for work in the fifth group.

BARIUM.

177. Occurrence and Preparation. — Barium occurs only in compounds, the chief of which are heavy spar, $BaSO_4$, and Witherite, $BaCO_3$.

This metal is not used in the arts. It is prepared by electrolyzing a thick paste of barium chloride and hydrochloric acid in the presence of mercury. The barium amalgam thus obtained is heated to expel the mercury, thus yielding a porous mass of metallic barium.

178. Properties and Compounds. — Barium burns in the air with great brilliancy. It forms some useful compounds.

(*a*) *Barium Oxide*, BaO, or baryta, is obtained by heating the nitrate until nitrous fumes cease to escape. From this oxide barium hydroxide, $Ba(OH)_2$, is prepared by the addition of water. Barium hydroxide is largely used in refining cane-sugar. Baryta water is the solution of this substance in water, which is used as a reagent.

(*b*) *Barium Chloride*, $BaCl_2$, is used in the laboratory as a reagent. It is prepared by dissolving barium carbonate in hydrochloric acid.

(*c*) *Barium Sulphate*, $BaSO_4$, is prepared for commerce by the reaction between barium chloride and sulphuric acid. It is used as a pigment and for weighting paper.

(*d*) *Barium Carbonate*, $BaCO_3$, is the precipitate obtained in analysis. It is soluble in acetic acid.

179. Tests for Barium. — 1. Insoluble solids are fused on charcoal with sodium carbonate and then dissolved in hydrochloric acid. The solution is tested by 2 and 3.

2. Solutions of barium salts are tested by the addition of reagents as follows : —

(*a*) Potassium dichromate and ammonia give the yellow precipitate, $BaCrO_4$, insoluble in acetic acid.

(*b*) Sulphuric acid gives the white insoluble precipitate, $BaSO_4$.

3. Barium salts tinge the Bunsen flame green when they are heated on a loop of platinum wire.

STRONTIUM.

180. Occurrence and Preparation. — Strontium occurs most plentifully in the minerals, celestine, $SrSO_4$, and strontianite, $SrCO_3$. The metal is prepared in the same way as barium, excepting that the amalgam is heated in a current of hydrogen.

181. Properties and Compounds. — Strontium is a yellow, malleable metal that oxidizes on exposure to the air, and which burns brilliantly when heated. It is not used in the arts.

Its principal compound which is of use is the nitrate, $Sr(NO_3)_2$. This salt is prepared by acting on strontium carbonate with nitric acid. Its principal use is as an ingredient of red fire for tableaux, etc.

A good mixture for red fire is made by pulverizing separately equal parts of dried strontium nitrate and potassium chlorate. These substances are then placed on a sheet of paper and an equal bulk of powdered gum-shellac is added. The whole is now thoroughly mixed with a

spatula. Friction or concussion must be avoided, as the mixture is explosive.

182. Tests for Strontium.—1. Strontium may be detected in any compound by fusing it on charcoal with sodium carbonate, after which the fused mass is dissolved in a few drops of hydrochloric acid. A platinum loop dipped in the solution colors the Bunsen flame crimson.

2. In its precipitates with most reagents strontium resembles barium. But it may be separated from the latter

FIG. 31.

metal by potassium dichromate, which gives the precipitate, $BaCrO_4$. If this precipitate be filtered out, the strontium may be precipitated from the filtrate as the sulphate, $SrSO_4$, by the addition of sulphuric acid. This precipitate is then tested by 1.

NOTE. Care must be used not to mistake the pale, yellowish red color of the calcium flame for that of strontium.

CALCIUM.

183. Occurrence and Preparation.— Calcium occurs widely distributed in compounds, of which the carbonate, $CaCO_3$, is the most plentiful. Iceland spar is a beautiful variety of this carbonate, possessing the property of double refrac-

tion (Fig. 31). Other crystalline forms are calc spar, marble, and dog-tooth spar. The amorphous varieties are known as limestone and chalk. Shells and corals are also mostly calcium carbonate. Calcium sulphate, $CaSO_4$, occurs in gypsum, anhydrite, and selenite.

This metal is not used in the arts, and is prepared in the same way as barium and strontium.

184. Properties and Compounds. — Calcium is a malleable metal which is not permanent in the air, and which burns with an orange-yellow light. The compounds of calcium are numerous and useful. A few of these compounds are noted.

FIG. 32.

(*a*) *Calcium Oxide*, CaO, or quicklime, is prepared by roasting the carbonate in lime-kilns (Fig. 32). It is used extensively for making mortar and other kindred purposes. When treated with water, calcium hydroxide, $Ca(OH)_2$, is obtained. This is used as a reagent. Lime containing about ten per cent of silica is used as a hydraulic cement, since it has the property of setting under water.

(*b*) *Gypsum*, $CaSO_4 + 2 H_2O$, occurs native and is much used as land-plaster. When burned, it yields plaster of paris.

(*c*) *Calcium Chloride*, $CaCl_2$, is obtained by treating limestone with hydrochloric acid. It is used in the laboratory as a dryer for gases.

(*d*) *Bleaching-powder* is obtained by passing chlorine gas into large chambers containing slaked lime. Its uses are familiar to all.

(e) *Calcium Carbonate*, $CaCO_3$, has already been mentioned. Almost every surface water contains this substance in solution. It is the principal substance which makes waters "hard." Its action depends upon the fact that it replaces the sodium or potassium of the soap and forms a lime soap which is insoluble. A lather cannot be obtained in a hard water until all the hardness is thus precipitated.

185. Tests for Calcium. — 1. A solid is first treated with hydrochloric acid and then tested by the flame-test. It gives an orange-red flame.

2. A solution of a calcium salt gives a white precipitate with ammonium carbonate, etc., the same as barium and strontium. By adding potassium sulphate to a solution containing all three metals in solution, barium and strontium may be precipitated and filtered out. From the filtrate calcium is then precipitated by ammonium oxalate, $(NH_4)_2C_2O_4$. A white precipitate, CaC_2O_4, is obtained.

MAGNESIUM.

186. Occurrence and Preparation. — Magnesium compounds are widely distributed. Magnesium sulphate, $MgSO_4$, is a constituent of many bitter waters. In small quantities it occurs in a greater part of our drinking-waters. Magnesite, $MgCO_3$, and dolomite, $CaMg(CO_3)_2$, are quite common compounds. Asbestos, $(MgCa)SiO_3$, talc, $Mg_3H_2(SiO_3)_4$, and meerschaum, $Mg_2H_2(SiO_3)_3$, are well known.

Magnesium is prepared for commerce by fusing a mixture of the dry chloride, fluorspar and metallic sodium in a closed crucible. The metal thus obtained is purified by

distillation. When in a semi-molten condition it is drawn into wire, which usually is finally flattened to form the magnesium ribbon of commerce.

187. Properties and Compounds. — Magnesium is a silver-white metal which is quite permanent in dry air. It burns readily, emitting a painfully bright and dazzling light that is rich in chemical rays. It is used in photography for illuminating dark places, such a caverns, in order that they may be photographed. It is also employed in pyrotechnics and for signaling.

(*a*) *Magnesia*, MgO, is obtained by igniting the carbonate. It is used in medicine.

(*b*) *Magnesium Chloride*, $MgCl_2$, is obtained from sea-water and from salt wells. It is used in dressing cotton goods.

(*c*) *Magnesium Sulphate*, $MgSO_4$, is known as Epsom salts. It is obtained from the waters of some springs. It is also prepared by treating the carbonate with sulphuric acid. It is much used as a cathartic and in dressing cotton goods.

(*d*) *Magnesium Carbonate*, $MgCO_3$, is obtained from dolomite. It is used in medicine; it also is used as a face-powder.

188. Test for Magnesium. — After removing the other fourth group metals with ammonia, ammonium chloride, and ammonium carbonate, magnesium may be obtained as a white crystalline precipitate, $MgNH_4PO_4$, by adding to the filtrate disodium phosphate. Under these circumstances no further test is necessary.

SEPARATION OF THE FOURTH GROUP METALS.

189. Barium, strontium, and calcium are precipitated as the carbonates, $BaCO_3$, $SrCO_3$, and $CaCO_3$, as explained in Art. 176. The precipitate is then filtered out, and magnesium is precipitated, as explained in the same article. If a precipitate is obtained in that place, no further identification of magnesium is necessary.

The precipitate containing the first three metals is first dissolved in acetic acid. The solution obtained is then treated as follows : —

(*a*) To the solution add ammonia till alkaline ; then add potassium dichromate. If barium be present, it will be precipitated as barium chromate, $BaCrO_4$. Filter. Dissolve the precipitate in hydrochloric acid and then add sulphuric acid; a white precipitate, $BaSO_4$, insoluble in acids, confirms the presence of barium.

(*b*) To the filtrate from (*a*) add potassium sulphate. A white precipitate, $SrSO_4$, indicates the presence of strontium. Filter. Test the precipitate by Art. 182, 1, to make sure strontium is present.

(*c*) To the filtrate from (*b*) add ammonium oxalate, $(NH_4)_2C_2O_4$. A white precipitate in this place insures the presence of calcium.

NOTE. If no barium be present, it is best not to add the potassium dichromate. By testing a small portion of the acetic acid solution for barium, the presence or absence of that metal may be determined.

CHAPTER XIV.

THE FIFTH GROUP METALS.

190.   The fifth group metals are often called the " Metals of the Alkalies." They do not furnish precipitates with ordinary reagents; but they are detected by the color of the flame obtained when any of their salts are placed in the Bunsen flame on a platinum loop.

In case other metals are in the solution, they must all be removed except magnesium, as explained in Art. 176.

POTASSIUM.

191. Occurrence and Preparation. — The potassium compounds are widely distributed. They occur in sea-water, in many mineral waters, and in all fruitful soils. They form essential constituents of plants. Sylvite, KCl; saltpetre, KNO_3; and potassium sulphate, K_2SO_4, are some of the most commonly occurring compounds. But potassium is also a constituent of many of the older rocks, in which it occurs in orthoclase.

In preparing potassium for commerce, acid potassium tartrate is first heated in closed iron retorts. This gives an intimate mixture of potassium carbonate and carbon.

This mixture is now placed in iron tubes covered with fire-clay, and then placed in a furnace and heated to a white heat (Fig. 33). Metallic potassium is obtained in the form of a vapor, which is condensed in a shallow box condenser placed outside the furnace. While in a liquid state it flows into vessels containing rock oil.
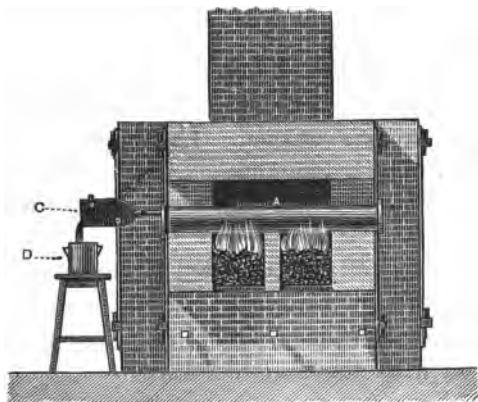
FIG. 33.

A is the iron tube retort coated with clay.
C is the condenser.
D is the cup containing rock oil.

192. Properties and Compounds of Potassium. — Potassium is a silver-white metal when first cut, but it soon shows a bluish surface on exposure. It ignites at a low temperature, and must be handled with pincers. It decomposes water at ordinary temperatures, often with explosive violence, hydrogen being liberated and potassium hydroxide being formed.

The potassium salts are highly valued, owing to their solubility in water and their adaptability for various medi-

cinal and industrial uses. The potassium salt of nearly every acid is an article of commerce. Space allows but few compounds to be mentioned.

(*a*) *Potassium Hydroxide*, or caustic potash, KOH, is prepared by treating potassium carbonate with slaked lime. The crude article is much used as a lye. The form employed for laboratory work is purified before it is cast into sticks.

(*b*) *Potassium Iodide*, KI, is obtained from a warm, concentrated solution of potassium hydroxide by adding iodine until the potassium is satisfied. The salt obtained is ignited to decompose any iodate that may be formed. The bromide, KBr, is obtained in a similar way by the use of liquid bromine.

(*c*) *Potassium Chlorate*, $KClO_3$, is obtained by passing chlorine gas through a solution of calcium hydroxide until calcium chlorate is formed. That salt is then decomposed by treatment with potassium chloride : —

$$Ca(ClO_3)_2 + 2\,KCl = CaCl_2 + 2\,KClO_3.$$
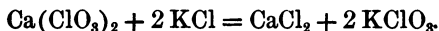
(*d*) *Potassium Nitrate*, or saltpetre, KNO_3, occurs as an incrustation on the soil in some hot, dry countries, as in India and Egypt. It is produced through the agency of minute organisms or ferments which cause the nitrogen of organic substances to combine with the potassium compounds of the soil. In the "saltpetre plantations" heaps of refuse animal matter are mixed with wood ashes and lime, and then moistened with urine or stable drainings. At intervals the outer layer is removed and leached with water to extract the nitrate.

This useful compound is also obtained by treating Chili saltpetre with potassium chloride : —

$$NaNO_3 + KCl = KNO_3 + NaCl.$$
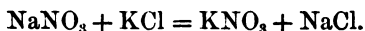
Potassium nitrate is extensively used in the manufacture of gunpowder, which is an intimate mixture of potassium nitrate, sulphur, and pulverized charcoal. In the laboratory this salt is used in many ways, as demonstrated by work previously done.

(*e*) *Potassium Carbonate*, or potash, K_2CO_3, is obtained by leaching wood ashes. The solution is evaporated to saturation, when this salt crystallizes out in impure forms, which are afterward purified by roasting in a reverberatory furnace.

193. Tests for Potassium. — Potassium compounds on a platinum loop color the Bunsen flame violet. This flame is visible through thick blue glass.

SODIUM.

194. Occurrence and Preparation. — Sodium is distributed everywhere. The most plentiful compound is the chloride, or common salt. Salt is obtained from sea-water and from salt wells in various parts of the world. Vast deposits of rock salt are found in different places. The brine from salt wells is pumped into large evaporating-pans heated by steam coils. When the brine is sufficiently concentrated, crystals of salt separate out, and these are removed from the mother liquors by means of perforated scoops.

Rock salt is usually mined; but at Marine City, Mich., the deposits are too deep for that method. Therefore wells are bored down to the salt rock, and streams of water are forced in. When this water has become saturated, it is raised into pans and evaporated the same as any brine.

In the United States salt is manufactured at Syracuse,

N.Y., and in the Saginaw Valley, Mich. Other localities also afford salt in smaller quantities.

Sodium is prepared in the same way as potassium, except that the carbonate and charcoal are employed in the reduction.

195. Properties and Compounds. — Sodium is a metal closely resembling potassium in its physical and chemical properties, but it is not so energetic in its action upon water. It will take fire in warm water, in starch paste, or on wet paper.

The compounds of sodium are as numerous and as useful as those of potassium. The salts are prepared by about the same methods, and their uses are similar to the potassium salts. But the sodium salts are not so well adapted for some uses. Thus, sodium nitrate does not make good gunpowder, owing to its greater liability to effloresce and to attract moisture. Again, many chemists prefer the potassium salts as reagents, since they do not " creep " out between the stopper and the neck of the bottle so much as the sodium compounds.

Many sodium compounds have already been noticed, and the limits of this work will warrant a notice of but few others.

(a) *Sodium Carbonate*, Na_2CO_3, is extensively used for various purposes. It is obtained from common salt by first converting the chloride into sodium sulphate by means of sulphuric acid. The sulphate is next heated with powdered coal, when it is reduced to sodium sulphide ; then this sulphide is heated with limestone, when it is converted into the carbonate. Usually the coal and limestone are added at the same time. The sodium carbonate thus obtained is now removed by lixiviation with water, after

which the solution is evaporated to dryness and then calcined, when it is ready for the market.

The *ammonia process* for making sodium carbonate is now extensively used. In this process sodium chloride is simply treated with ammonia and carbon dioxide. Acid sodium carbonate, $NaHCO_3$, is first formed. Then this compound is decomposed by heat into the normal carbonate and carbon dioxide.

Soda crystals or sal sodæ, $Na_2CO_3 + 10 H_2O$, is obtained by allowing the common carbonate to crystallize out of a water solution. It is used in softening water.

Acid sodium carbonate, $NaHCO_3$, is used for domestic purposes as saleratus and as an ingredient of baking-powders. It is often called bicarbonate of soda.

(*b*) Glass is a silicate of calcium and sodium or of calcium and potassium. Ordinary glass contains sodium. The difficultly fusible Bohemian glass contains potassium. Glass used for optical purposes and for making some kinds of fine glassware contains lead. Green bottle glass owes its color to the presence of iron.

Ordinary glass is made by fusing a mixture of quartz, quicklime, and sodium carbonate. Sometimes limestone is used in place of the quicklime.

196. Test for Sodium. — Any sodium compound on the platinum loop colors the Bunsen flame yellow. This flame is not visible through the blue glass.

<div align="center">AMMONIUM.</div>

197. Ammonium is a hypothetical compound, NH_4, which resembles a metal in some respects. We have already seen how this combines with acids to form salts. Thus,

we have had ammonium chloride, NH_4Cl, ammonium nitrate, NH_4NO_3, and other salts. Again, it seems that ammonium is capable of forming an amalgam with mercury, which may be prepared by adding sodium amalgam containing from one to three per cent of sodium, to a strong solution of ammonium chloride. But notwithstanding these considerations, ammonium has not been isolated.

The ammonium salts may usually be made by adding the acid directly to ammonia, NH_3. In the case of ammonium carbonate, $(NH_4)_2CO_3$, ammonium chloride is sublimed with calcium carbonate, after which the product is digested with strong aqua ammoniæ.

Ammonium sulphide, $(NH_4)_2S$, is obtained in the laboratory for reagent purposes by passing hydrogen sulphide through reagent ammonia until it will not give a precipitate with a solution of magnesium sulphate. Upon standing, this sulphide changes to the yellow ammonium sulphide, $(NH_4)_2Sx$, spoken of in the second group metals. This yellow sulphide may also be obtained by warming ordinary ammonium sulphide with flowers of sulphur; the operation may be conducted in a test-tube, and the reagent may be prepared in small quantities from time to time as needed.

IDENTIFICATION OF THE FIFTH GROUP METALS.

198. Both sodium and potassium are detected by the flame-test. If both are present, the yellow sodium flame is liable to obscure the potassium flame. But when viewed through the blue glass, the sodium flame is shut off while the potassium flame remains visible.

Ammonium is always to be sought in the original solution. In the course of analysis so much ammonia is em-

ployed that the solution tested for sodium and potassium would always give the test for ammonium.

Therefore add potassium hydroxide to the original solution, warm gently, and test the escaping fumes for ammonia by the odor, and with a glass rod moistened with hydrochloric acid, etc., as in Art. 33.

ANALYSIS OF AN UNKNOWN SUBSTANCE.

I.

TO DISSOLVE A SOLID.

199. If the unknown be in solution, proceed immediately by II. If the substance be a solid (excepting such a substance as sulphur or iodine), it is best to bring it into solution. This is not always easy to do, and some methodical plan ought to be followed, such as the one here given : —

1. Place the substance in an evaporating-dish, add *water*, and boil. If the substance dissolve completely, treat the solution by II. If it be doubtful whether any of the substance has dissolved, evaporate carefully to dryness (on a piece of porcelain or on platinum foil) a few drops of the liquid in the dish. If a residue remain, some of the substance has dissolved. Filter out the solid remaining in the evaporating-dish, and treat the filtrate as in II.; proceed by 2 with the remaining solid.

If none of the solid has dissolved, proceed with it by 2.

2. Add *nitric acid* to the contents of the evaporating-dish, and boil gently. If the substance dissolve completely, evaporate the solution nearly to dryness to expel any excess of acid ; dissolve the residue in water, and treat the solution by II.

If it be doubtful whether any of the substance has dis-

solved, test a few drops on porcelain as before. If a part has dissolved, filter, evaporate the filtrate to expel any excess of acid, add water, and then proceed by II. Treat the residue by 3.

If none of the substance has dissolved, treat the solid by 3.

3. Add *nitro-hydrochloric acid* to the contents of the evaporating-dish, and warm gently. If the substance dissolve completely, expel the excess of acid, etc., as in 2.

If it be doubtful whether any of the substance has dissolved, test on porcelain, etc., as before.

If a portion of the solid dissolve, filter, expel any excess of acid, etc., as before. Treat the residue by 4.

If none of the substance has dissolved, it is insoluble in acids, and must be treated as in 4.

4. Fuse the insoluble substance on charcoal with sodium carbonate, and then commence back again by 1. The mass will usually dissolve either in water or in nitric acid.

In fusing, note any coating around the assay.

II.

SEPARATION AND DETECTION OF BASES.

1. Add *hydrochloric acid* to the solution; a white precipitate indicates any or all of the first group metals in the form of the chlorides: $PbCl_2$; $AgCl$; Hg_2Cl_2. Filter out the precipitate, and proceed with it as by Art. 131. Treat the filtrate by 2.

2. Through the filtrate from 2 pass *hydrogen sulphide* for a long time. A precipitate may contain any or all of the second group metals in the form of the sulphides: As_2S_3 (yellow); Sb_2S_3 or Sb_2S_5 (orange); SnS (brown);

SnS_2 (yellow); Bi_2S_3 (black); CuS (black); CdS (yellow); PbS (black); HgS (black).

Filter, and treat the precipitate by Art. 150. Boil the filtrate to expel all hydrogen sulphide, add a few drops of nitric acid, boil again for a short time, and proceed by 3.

3. To the prepared filtrate from 2 add *ammonia and ammonium chloride;* any precipitate may be: $Fe_2(OH)_6$ (reddish brown); $Cr_2(OH)_6$ (bluish green); $Al_2(OH)_6$ (white, gelatinous). Filter. Treat the precipitate by Art. 175, I.

To the filtrate add *ammonium sulphide.* Any precipitate may be: MnS (flesh-colored); CoS (black); NiS (black); ZnS (white). Filter, and treat the precipitate by Art. 175, II.

Evaporate the filtrate to dryness, gently ignite the residue to expel as much of the reagents previously added as possible, dissolve the residue in water, and proceed by 4.

4. To the prepared filtrate from 3 add *ammonia, ammonium chloride,* and *ammonium carbonate.* A precipitate may be the carbonates (white): $BaCO_3$; $SrCO_3$; $CaCO_3$. Filter, and test the precipitate by Art. 189. Divide the filtrate in two parts; to one of these parts add *disodium phosphate;* a white precipitate, NH_4MgPO_4, identifies magnesium.

5. Test the second part of the filtrate from 4 by Art. 198. Test the original solutions for ammonium by Art. 33.

III.

DETECTION OF ACIDS.

1. If the unknown is a solution or a solid soluble in water and has been found by the work in II. to contain

arsenic, chromium, or manganese, these elements may be present in the unknown as acids. Therefore test the substance for the acids formed by these elements.

2. If these metals are not present, but other metals belonging to any group (except the fifth group metals and magnesium) have been found, it is necessary to remove these bases before testing for acids. This is accomplished by adding to the solution, potassium hydroxide and potassium carbonate. These reagents remove all metals that would interfere with the tests for acids. Filter out the precipitate, and treat the filtrate by (a), etc. If no bases are present in the solution that interfere with the acid tests, proceed by (a), etc.

(a) Acidulate a portion of the solution or filtrate with nitric acid and add barium chloride, $BaCl_2$. A white precipitate, $BaSO_4$, shows that sulphuric acid is present.

(b) Acidulate a second portion of the solution or filtrate with nitric acid and add silver nitrate. A white precipitate indicates the presence of any of these acids: HCl; HBr; HI, HCN.[1] Therefore to a fresh portion of the solution or filtrate add hydrochloric acid, chlorine water, and carbon disulphide, and shake. No color indicates HCl or HCN. Try the odor of the unknown; an odor of peach blossoms indicates HCN; test further by Art. 93. If no odor is noticeable, the work up to this point shows hydrochloric acid, HCl, to be present.

If the carbon bisulphide is colored brownish red, HBr is present. If the color is violet, HI is present.

(c) Acidulate a third portion of the solution or filtrate

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[1] $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$ would give precipitates here. But the student would probably discover these acids while working for the bases. If indications of these acids are observed, test by Art. 156, 2 and 3.

with hydrochloric acid, and test for nitric acid, Art. 42. (See note.)

(d) If carbonic acid be present, it may be found by adding to the original substance hydrochloric acid. A brisk effervescence will ensue.

(e) Now test separate portions of the solution, or filtrate for the following acids: H_3PO_4; H_4SiO_4; H_3BO_3; $H_2S_2O_3$; $HClO_3$.

3. If the substance be an oxide or a hydroxide, it will give no tests for acids.

4. If the substance be in the form of a powder or a solid, one may tell nearly what acids are present by placing some of the dry powder in a test-tube and adding sulphuric acid. Upon heating gently the following phenomena may occur : —

(a) A rapid effervescence of an odorless, colorless gas indicates a carbonate.

(b) A slower effervescence of a colorless gas possessing the odor of rotten eggs indicates a sulphide. An odor of burning matches indicates a sulphite or a thio-sulphate. An odor of peach blossoms indicates a cyanide. An odor of vinegar indicates an acetate. An irritating odor indicates a chloride, a fluoride, or a nitrate.

(c) A colored gas with an irritating odor indicates an iodide or a bromide.

(d) A sudden explosion identifies a chlorate.

(e) If no action occurs, the acid may be H_2SO_4; H_3PO_4; H_4SiO_4; H_3BO_3. Therefore test for these acids in order.

NOTE. It must be distinctly understood that the scheme outlined in 4 only gives indications. These indications are not sufficiently positive to permit an acid (except chloric acid) to be reported without further tests. Therefore when an indication is obtained, turn to the acid indicated and make the tests there given.

CHAPTER XV.

200. Organic and Inorganic Substances. — In former times all compounds were classified into organic and inorganic substances. This classification was based upon the supposition that the so-called organic substances could be produced only through the intervention of living organisms, *i.e.* plants and animals. Starch, sugar, indigo, and urea will serve as examples of the so-called organic substances, while any of the salts or ores previously considered will afford examples of the inorganic compounds.

In these later days, however, so many of the so-called organic compounds have been prepared in the laboratory, by artificial processes, that it has become evident that the name " organic " is not at all appropriate, nor was the former distinction well taken. In short, even " Organic Chemistry," according to our better understanding, is now usually termed the Chemistry of the Carbon Compounds, or, better still, the Chemistry of the Hydrocarbons and their Derivatives.

The carbon compounds are almost innumerable in number; and they vary in their structure from simple forms to those of the greatest complexity. Carbon, as we have seen, is quadrivalent; and, moreover, it seems to possess the property of combining with itself to form centres, around which the remaining elements of the more complex compounds are held by the usual laws of valence. Thus it

appears that an infinite number of carbon compounds are possible, and that their complexity may be very great.

201. Homology. — At the outset it would seem desirable to arrange the carbon compounds, if possible, into classes, so that some order might be introduced into their consideration.   Fortunately, this may be done.   Thus, if we examine the formulæ of the compounds CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, etc., we shall see that there are evident relations existing.   In the first place, it appears that between any consecutive two of these compounds there is a constant difference in composition of CH_2; and in the second place, it is evident that these compounds form a natural series, all members of which may be represented by one general formula.   Thus, C_nH_{2n+2} will represent any member in the foregoing series.   This series is a well-known one, and is called the marsh gas, or paraffin, series.   Such a relation between compounds is termed *Homology*, and such a series is called a *Homologous Series*.

In all there are at present known, to a greater or less extent, about eighteen of these homologous series; and it matters not what one of the numerous compounds of carbon may be under consideration, nor how complex its structure may be, it can usually be assigned to some one of these series.   Some compounds, however, belong to more than one series.

In the following article a table is given for inspection which gives the names of these different series, together with some other facts that will be useful.

If we begin with the lowest member of any of these homologous series and add successively CH_2, it is evident that the series is capable of extension to infinity.   But as a matter of fact, the number of hydrocarbons in any series,

so far as known, is quite limited.   In the first, or paraffin, series, CH_4, C_2H_6, etc., the series is known to extend to $C_{35}H_{72}$, and sixteen terms have been described.   In several other series but one member is known, while still others have but from two to four representatives.   In the sixteenth series not a single term is known.   But these series are important, since their different members are now considered to be the starting-points from which all the various compounds are derived.   It will be noticed that these substances contain carbon and hydrogen only, and in general they are termed *Hydrocarbons*.

202.   A Table of the Hydrocarbon Series.

Name of Series.	General Formula.	Lowest Member known.	Formula Lowest Member.
Paraffin	C_nH_{2n+2}	Methane	CH_4
Olefine	C_nH_{2n}	Ethylene	C_2H_4
Acetylene	C_nH_{2n-2}	Acetylene	C_2H_2
Terpene	C_nH_{2n-4}	Valylene	C_5H_6
Benzene	C_nH_{2n-6}	Benzene	C_6H_6
Cinnamene, or Styrene . .	C_nH_{2n-8}	Styrene	C_8H_6
Acetenyl-Benzene	C_nH_{2n-10}	Phenyl-Acetylene	C_8H_6
Naphthalene	C_nH_{2n-12}	Naphthalene	$C_{10}H_8$
Diphenyl	C_nH_{2n-14}	Diphenyl	$C_{12}H_{10}$
Stilbene	C_nH_{2n-16}	Acetylene-Naphthalene	$C_{12}H_8$
Anthracene	C_nH_{2n-18}	Anthracene	$C_{14}H_{10}$
Benzyl-Naphthalene . . .	C_nH_{2n-20}	Benzyl-Naphthalene	$C_{17}H_{14}$
Pyrene	C_nH_{2n-22}	Pyrene	$C_{16}H_{10}$
Chrysene	C_nH_{2n-24}	Chrysene	$C_{18}H_{12}$
Dinaphthyl	C_nH_{2n-26}	Dinaphthyl	$C_{20}H_{14}$
——	C_nH_{2n-28}	——	—
Idrialene	C_nH_{2n-30}	Idrialene	$C_{22}H_{14}$
Tetraphenyl-Ethylene . .	C_nH_{2n-32}	Tetraphenyl-Ethylene	$C_{26}H_{20}$

203. Names of the Members of the Hydrocarbon Series. — In the first or paraffin, series, the ending " ane " is used as a distinctive ending, while in all other series the names of the members usually end in " ene." In the first two series, after the first four members, the numeral prefixes, " pent," " hex," " sept," etc., are used to distinguish the different compounds. The subjoined lists will illustrate the principles used in naming the first two series : —

PARAFFIN SERIES.		OLEFINE SERIES.	
C_nH_{2n+2}.		C_nH_{2n}.	
CH_4 . . .	Methane.	C_2H_4 . . .	Ethylene.
C_2H_6 . . .	Ethane.	C_3H_6 . . .	Propylene.
C_3H_8 . . .	Propane.	C_4H_8 . . .	Butylene.
C_4H_{10} . . .	Butane.	C_5H_{10} . . .	Amylene.
C_5H_{12} . . .	Pentane.	C_6H_{12} . . .	Hexylene.
C_6H_{14} . . .	Hexane.	C_7H_{14} . . .	Heptylene.
Etc., etc.		Etc., etc.	

In naming the members of the remaining series, no such regular method has been followed. The names are mostly compounded from simpler ones which correspond to simple radicals, of which the higher series may be said to be composed. When the names are not compound, they frequently indicate the source from which the member is obtained, or some striking peculiarity belonging to that member. But it is not necessary for the beginner to master all these names. Some of the most important will be noticed in appropriate places.

204. Elementals and Derivatives. — In the previous chapters of this work we were dealing with elements and with the compounds formed by the union of these elements. A somewhat similar distinction may be made in the study of

the carbon compounds. It is now customary to consider those hydrocarbons which form the members of the different homologous series as primary compounds. The more complex compounds, which contain other elements besides carbon and hydrogen, are regarded as derivatives of the simpler hydrocarbons. The principal derivatives are of four kinds:—

1. Those containing chlorine, bromine, and iodine. These are termed in general the *Halogen Derivatives.*

2. Those containing oxygen. Under this division are included such important compounds as the *Alcohols, Ethers,* and *Acids.*

3. Those containing nitrogen. These are formed by the reaction between certain hydrocarbons and such reagents as nitric acid and ammonia and cyanogen. Those obtained from ammonia are termed *Amines; e.g.* NH_2CH_3, methylamine. Those from nitric acid and cyanogen are called respectively *Nitro* and *Cyano Derivatives.*

4. Those containing sulphur. Here are included such compounds as the *Mercaptans* and the *Sulphonic Acids.*

205. Substitution. — In the paraffin series the carbon atoms are saturated, *i.e.* each of the four bonds of carbon holds in combination an atom of hydrogen. This may be graphically represented, in the case of methane, thus:

$$H - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - H.$$

Ethane may be represented thus:

$$H - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - H.$$

Propane may be represented thus:

$$H - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - H.$$

Now,
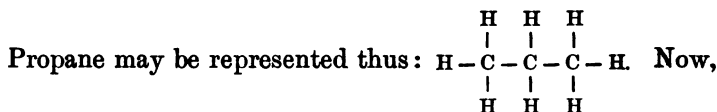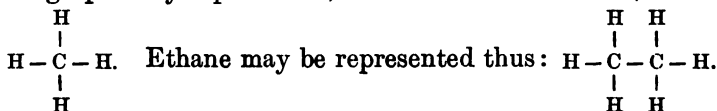
since the carbon atoms can hold no more elements in combination, nothing can be directly added to any of the hydro-

carbons of the paraffin series.   But when any one of these compounds is treated with the proper reagents, one or more atoms of hydrogen may be displaced, and another element taken instead.   Thus, if methane be mixed with chlorine gas, and then exposed to the action of diffused sunlight, hydrochloric acid is given off, and different products are obtained, depending upon the duration of the action.   Thus the following four compounds have been isolated, by re-placing the hydrogen in methane, CH_4: chlor-methane, CH_3Cl; dichlor-methane, CH_2Cl_2; trichlor-methane, $CHCl_3$; carbon tetra-chloride CCl_4.

In these derivatives it is plain that one after another of the hydrogen atoms has been displaced by chlorine.   The products thus obtained are called *Substitution Products;* and the process of substituting other atoms, or groups of atoms, for hydrogen is termed *Substitution.*

Bromine and iodine also form substitution products with methane.

Sug.   Student, write the formulæ of these products, and give their names.   Thus, CH_3Br, brom-methane ; CH_3I, iodo-methane.

Benzene, C_6H_6, of the benzene series, also furnishes a good illustration of the substitution products: C_6H_5Cl, $C_6H_4Cl_2$, $C_6H_3Cl_3$, $C_6H_2Cl_4$, C_6HCl_5, C_6Cl_6.

Sug.   Student, name these compounds, beginning with C_6H_5Cl, chlor-benzene.   Complete the series of substitution products for benzene, and give the names, beginning with $C_6H_5(NO_2)$, nitro-benzene, etc., etc.

206. Addition Products. — In the case of the olefine series, other elements may be directly added to the hydrocar-bons.   Ethylene can be represented by the graphic for-mula, $H_2 = C = C = H_2$, in which the carbon atoms are joined by two bonds.   When brought under the influence of the proper reagents, it seems as if two of these bonds

are released, thus enabling this hydrocarbon to act like a bivalent radical. Thus we have, from ethylene, C_2H_4: ethylene chloride, $C_2H_4Cl_2$; ethylene bromide, $C_2H_4Br_2$; ethylene hydrochloride, C_2H_4HCl; etc. Other series also afford examples of this method of derivation. Hydrocarbons that form addition products are often spoken of as unsaturated compounds.

207. Unsaturated Radicals in the Paraffin Series. — In the paraffin series such compounds as CH_3Cl, CH_3Br, C_2H_5Cl, C_2H_5Br, etc., occur, in which such radicals as CH_3 and C_2H_5 appear. These radicals have not been isolated, but their occurrence is so common that they have been assigned names ending in "yl." CH_3 is called *methyl*, and C_2H_5 is called *ethyl*. These radicals have one atom of hydrogen less than the primary compounds which gave them origin. Thus: —

Methane, CH_4 . . . Methyl, CH_3.
Ethane, C_2H_6 . . . . Ethyl, C_2H_5.
Propane, C_3H_8 . . . Propyl, C_3H_7.
Butane, C_4H_{10} . . . . Butyl, C_4H_9.
Etc., etc.   Etc., etc.

All these radicals are monovalent, and they act like univalent metals in forming salts. Thus we have methyl chloride, CH_3Cl; ethyl bromide, C_2H_5Br; propyl iodide, C_3H_7I; etc. Note that two methods of naming these compounds are in use. Thus CH_3Cl is called chlor-methane or methyl chloride.

Unsaturated primary compounds like the olefines are sometimes called radicals.

208. Isomerism. — Frequently one formula represents two or more entirely different substances. Each compound may contain exactly the same number of atoms of the different

elements, the molecular weights may be the same, and even the vapor densities may be identical. For example, C_2H_6O represents two entirely different substances. One is methyl oxide, $(CH_3)_2O$, a gas, and the other is ordinary alcohol, or ethyl hydroxide, C_2H_5OH. These two substances fulfil the foregoing conditions exactly, and are called *Isomers*. When two substances afford such a perfect case of isomerism, they are also called *Metameric Isomers*, to distinguish them from another form of isomerism in which the molecular weights of the different compounds vary by some multiple of the lowest member. Thus we have acetylene, C_2H_2; benzene, C_6H_6; and styrene, C_8H_8. These substances are called *Polymeric Isomers*. The C_nH_{2n} series of hydrocarbons affords good examples of polymerism.

209. Uniformity among Derivatives. — Each primary hydrocarbon is capable, in theory at least, of furnishing a set of derivatives similar to those obtainable from any other hydrocarbon. Thus, each hydrocarbon will furnish a set of halogen derivatives, — an alcohol, an ether, an acid, etc., etc. Hence it is not necessary, in order to obtain a general view of the principles involved in the chemistry of the carbon compounds, to study all the hydrocarbons and their derivatives in detail. The study of any one hydrocarbon series, such as the paraffin series, would answer this purpose.

It is true that the derivatives obtained even from hydrocarbons in the same series possess different physical and chemical characteristics, but it is also true that they possess in common many points of similarity. As a rule, with a reasonable number of exceptions, the general reactions and methods employed with one are applicable to all.

In the limited space at our disposal, only the most important compounds can be considered.

CHAPTER XVI.

THE PARAFFIN SERIES, C_nH_{2n+2}.

210. Occurrence and Preparation. — This series of hydro-carbons is often called the marsh gas or methane series from the name of its lowest member. Many of these primary hydrocarbons occur in crude petroleum and in gases occurring in connection with the coal deposits. Some of them, as well as some of their derivatives, are to be had from the destructive distillation of coal, wood, bones, and the refuse liquids or " vinasses " left after dis-tilling the fermented molasses obtained from beet sugar factories.

As a matter of interest, the paraffin series can be built up from the elements by synthetic processes. Thus, when water or hydrogen sulphide is mixed with carbon disul-phide (all of which can be prepared directly from the ele-ments), and the mixture passed over heated metals, such as copper, methane, CH_4, the first member is obtained: —

$$CS_2 + 2\,H_2O + 6\,Cu = CH_4 + 2\,Cu_2S + 2\,CuO.$$
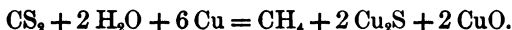
Now by treating methane with iodine, iodo-methane or methyl iodide, CH_3I, is to be had. Then when methyl iodide is treated with metallic sodium, the next member, ethane, C_2H_6, is produced: —

$$2\,CH_3I + 2\,Na = C_2H_6 + 2\,NaI.$$
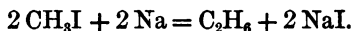
Next ethyl iodide, C_2H_5I, can be prepared from ethane; and when a mixture of this substance and methyl iodide is

treated with sodium, the next member, propane, C_3H_8, is to be had : —

$$CH_3I + C_2H_5I + 2Na = C_3H_8 + 2NaI.$$

Again, when ethyl iodide alone is treated with sodium, butane, C_4H_{10}, is produced.

$$2C_2H_5I + 2Na = C_4H_{10} + 2NaI.$$
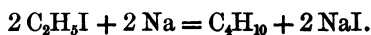
It can be readily seen that in this way it is possible to build up a large number of the members of this series. Other methods of synthesis are also known and employed.

Of course for commercial purposes resort is usually had to the natural sources of the·different compounds. But such synthetic processes are of interest and of value, since to them we owe much of our knowledge concerning the constitution of the carbon compounds. Moreover, a large range of possibilities is suggested in methods of building up compounds, which have of late borne many good results, since by these methods various substances of great utility have been produced by artificial means.

211. Properties of the Paraffins. — Beginning with methane, a gas, this series gradually passes into volatile liquids, heavy liquids, and finally into waxy solids at ordinary temperatures. It is from these solids, the paraffins, that the series obtains its name. Many useful and well-known substances belong to this series.

Among the gases is methane, or fire damp, which has already been described under carbon. Ethane and propane are also gases. Butane is a liquid boiling at 1° C. Pentane boils at 38° and hexane at 70° C. And so the series passes on up to the waxy solids known as "paraffin," which is a mixture of the higher hydrocarbons of this series.

Petroleum, or rock oil, has been mentioned as one of the

natural sources of this series. From this crude oil are obtained the commercial products, *cymogene, rhigoline, naphtha, gasoline, kerosene, lubricating oil*, and *paraffin*. All of these products are mixtures of different hydrocarbons.

In order to separate these substances the crude oil is subjected to distillation. Beginning with low temperatures the compounds, ethane, propane, and butane, which were dissolved in the crude oil, pass off first and are condensed under pressure to a liquid consisting principally of butane. This liquid is known as *cymogene*, and is used for the artificial production of low temperatures. Products obtained at about 18° F. are called *rhigoline*. From this point up to about 70° F. the volatile substances known as *naphtha, benzine, gasoline*, etc., are obtained. These are much used for heating and illuminating purposes, but special burners are required for their consumption. By means of a rotary air-pump that sends a current of air through a specially appointed tank holding gasoline, a very good quality of gas for illuminating and heating purposes is obtained. The use of gasoline in our modern gasoline stoves barely needs mentioning.

Above 170° F. kerosene oil is obtained, while at still higher temperatures a heavy lubricating oil is given off. The waxy residue is purified and sold under the name "paraffin." Vaselene, or cosmolene, is the more liquid portions of paraffin.

The kerosene obtained by distillation is colored and contains objectionable impurities. Consequently it is subjected to refining processes in which it is treated with sulphuric acid, alkalies, and water. Thus is obtained the water-white oil in such common use wherever gas is not available.

Kerosene that contains the more volatile hydrocarbons

is dangerous in that it has given rise to many disastrous conflagrations by exploding. The laws of nearly all countries now require it to be of a certain standard, which varies somewhat for different countries, and even in different parts of the same country. It is required to have a *flashing-point*, varying from 73° to 110° F., according to the locality, as illustrated in the following: —

Exp. 91. Arrange an apparatus as shown in Fig. 34. The glass cylinder A has a wooden cork in the bottom, and the bent glass tube *d* terminates in a fine jet at *b*. A large eight-inch test-tube having its bottom removed makes a good cylinder. The bottom may be cut off by first making a scratch with a file, and then by means of a ten-penny wire nail heated to low redness, a check can be started at the file mark and led squarely around the tube.
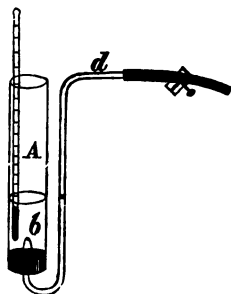
Fig. 34.

Fill the cylinder about one-third full of kerosene to be tested, and then place the apparatus in a water-bath (a tin can will answer) up to the level of the kerosene. Apply heat to the bath, and force a steady current of air through the bent tube until there is a half an inch or so of foam on the kerosene. At every rise of one degree on the thermometer apply a lighted taper to the mouth of the cylinder. When the flame flashes down to the kerosene, the reading of the thermometer gives the flashing-point.

Asphalt or *Asphaltum* is a solid related to the paraffins. It occurs in vast deposits, as at Trinidad. It is soluble in turpentine and in benzene, and is used as a paint, etc.

After this preliminary view of the paraffin series we will next consider methane and ethane and some of their most useful derivatives.

I. HALOGEN DERIVATIVES.

212. Chlor-Methane, or Methyl Chloride, CH_3Cl. — Chlor-methane has already been noticed as the first substitution product when methane and chlorine gas react.   Pure methyl chloride is prepared by treating a solution of zinc-methane, $Zn(CH_3)_2$ (Art. 223), and methyl alcohol, CH_3OH (Art. 215), with hydrochloric acid.

But the chlor-methane of commerce is now largely prepared from the destructive distillation products of the beet root vinasses.   Among these products is trimethylamine, $N(CH_3)_3$ (Art. 219).   This is treated with hydrochloric acid, and then subjected to heat.   The methyl chloride thus obtained is purified by treatment with hydrochloric acid, and then dried over calcium chloride.   It is then condensed under pressure and preserved in strong cylinders.

Methyl chloride is a mobile, ethereal-smelling liquid which boils at 23°.   It is now much used in making various aniline colors, and for refrigerating purposes.   It burns with a green-bordered flame.

213. Trichlor-Methane, or Chloroform, $CHCl_3$. — Of the remaining chlorine substitution products of methane, chloroform is the only one deserving mention here.   The substituting process is not applicable for the commercial production of chloroform.   In commerce several processes are employed.

EXP. 92.   Place a few crystals of chloral hydrate, $CCl_3.CH(OH)_2$, in a test-tube, add a concentrated solution of potassium hydroxide, KOH, and warm gently.   Note the odor

of the chloroform produced. In addition to the chloroform potassium formate is formed : —

$$CCl_3.CH(OH)_2 + KOH = CHCl_3 + CHKO_2 + H_2O.$$
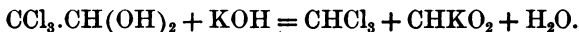
Large quantities of chloroform are manufactured in this way, excepting that sodium hydroxide is used instead of the potassium compound.

Another method extensively employed is to treat common alcohol with bleaching-powder. The reactions involved are complicated, and cannot well be represented by one equation.

Chloroform is a colorless, mobile liquid which possesses a characteristic and penetrating odor. Its specific gravity is 1.525. It mixes with alcohol and ether, but not with water. It acts as a solvent on many oils, gums, resins, and alkaloids. Hence it is much used in the arts and for analytical purposes.

Chloroform is extensively used in medicine and in surgery as an anæsthetic.

214. Tri-iodo-Methane, or Iodoform, CHI_3. — Iodoform is a yellowish solid which crystallizes in six-sided plates. This is the most important of the iodine substitution products of methane. It can be prepared by the action of iodine on ethyl alcohol, in the pressure of an alkali, or an alkaline carbonate.

Exp. 93. Dissolve 10^g crystallized sodium carbonate in 50^{cc} water, add about 6^{cc} common alcohol, and warm up to about 70° C. Now slowly add 5^g iodine and agitate. Note the crystals of iodoform that separate out. Remove the crystals by filtration; dry them between pieces of blotting-paper. Note their odor and their other characteristics.

The preceding experiment illustrates the commercial processes involved in the manufacture of iodoform, but

some of the by-products obtained along with the iodoform are so treated that a part of them is also converted into iodoform. Other materials and processes are also employed. If we use potassium hydroxide instead of the sodium carbonate, the principal reactions may be represented thus : —

$$CH_3.CH_2OH + 4I_2 + 6KOH = CHI_3 + CHKO_2 + 5KI + 5H_2O.$$
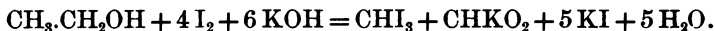
Iodoform has an odor resembling saffron; it is insoluble in water, but soluble in alcohol. It is used in medicine and in surgery. It has an anæsthetic action, especially upon the muscles, even when applied locally.

II. OXYGEN DERIVATIVES.

215. Methyl Alcohol, or Wood Alcohol, CH_3OH. — This compound is an important one both from a theoretical and from a practical standpoint. In the first place, it is a type of a number of alcohols, and bears the same relation to methane that any other primary alcohol does to the hydrocarbon from which it is derived. An alcohol is a hydroxide of a primary hydrocarbon obtained by replacing one atom of hydrogen by the radical hydroxyl, OH. Thus methane, CH_4, or CH_3H, yields methyl alcohol CH_3OH.

Methyl alcohol does not occur free in nature, but one of its salts, methyl salicylate, $CH_3C_7H_5O_3$, occurs ready formed in the oil of wintergreen, *Gaultheria procumbens.*

The principal method of obtaining this alcohol is the recovery of the alcohol produced by the dry distillation of wood and of beet root vinasses. Other products, such as tarry substances and acetic acid, are obtained at the same time. These mixtures are first distilled, when what little methyl alcohol is present is found in the first portions of

the distillate. The crude spirit is next treated with quick-lime, caustic soda, and a weak oxidizing reagent in order to destroy some of the accompanying impurities. Next it is subjected to a systematic course of fractional distillation (see Art. 225), when the wood alcohol of commerce is obtained.

In order to obtain pure methyl alcohol, the commercial article is treated with oxalic acid, which produces the solid substance methyl oxalate, $(CH_3)_2C_2O_4$. This compound when treated with water yields the pure spirit and oxalic acid.

Methyl alcohol can be built up by synthetical reactions, but these are of scientific interest only.

This alcohol is a mobile liquid of a pleasant, vinous odor, and it finds employment for many mechanical purposes, and for preparing the aniline colors.

216. Methyl Ether, $(CH_3)_2O$. — This compound is also a type of an important class of substances, the ethers. A simple ether is really an oxide of an unsaturated radical, such as methyl, CH_3; ethyl, C_2H_5; etc. These ethers may be considered as derived from alcohols by replacing the hydrogen of hydroxyl by the alcohol radical. Thus from methyl alcohol, CH_3-O-H, we get methyl ether, CH_3-O-CH_3.

In practice, methyl ether is obtained by acting on methyl alcohol by strong sulphuric acid. A mixture of these substances is made of the specific gravity 1.29. This mixture is heated from 125° to 128°, and never above 130°, when the ether is regularly given off. The process is made continuous by adding enough of the alcohol from time to time to bring the mixture back to the required specific gravity.

Methyl ether is a gas having a pleasant odor. It is condensed to a liquid by means of pressure, and used in large quantities for refrigerating purposes.

217. Methyl Aldehyde, or Formic Aldehyde, CH_2O. — This substance is also typical of a class of compounds yielded by each hydrocarbon. An aldehyde is obtained by gently oxidizing an alcohol. When vapors of methyl alcohol and air are brought in contact with a glowing platinum spiral, the following reaction occurs : —

$$CH_3OH + O = CH_2O + H_2O.$$
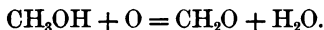
Methyl aldehyde has a peculiar and penetrating odor. It has been prepared in dilute solutions only.

218. Formic Acid, CH_2O_2. — When the oxidation of methyl alcohol is carried farther than in the case of methyl aldehyde, two atoms of hydrogen are withdrawn from each molecule of the alcohol, and formic acid is produced : —

$$CH_3OH + 2 O = CH_2O_2 + H_2O.$$
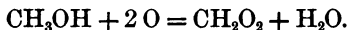
Each primary alcohol has a corresponding acid.

This acid occurs ready formed in the bodies of red ants, in stinging nettles, in tamarinds, and in the shoots of various pines.

It may be prepared in many ways as by the distillation and oxidation of various organic substances. But it is now principally obtained by heating oxalic acid : —

$$C_2H_2O_4 = CH_2O_2 + CO_2.$$

In practice, the acid is mixed with anhydrous glycerine, and the details are so arranged that the process becomes continuous. The reactions are somewhat complicated.

This acid is a colorless liquid which emits fumes of a penetrating acid odor. It acts so violently on the skin

that one or two drops produce extreme pain and leave painful white blisters. With the metals it forms a series of salts, the formates, in which it plays the part of an ordinary monobasic acid.

III. NITROGEN DERIVATIVES.

1. *Substituted Ammonias, or Amines.*

219. The Methylamines. — Ammonia can be made to give up one, two, or three of its hydrogen atoms and take in place thereof one, two, or three unsaturated hydrocarbon radicals. Thus we have ammonia, NH_3; methylamine, NH_2CH_3[1]; dimethylamine, $NH(CH_3)_2$; and trimethylamine, $N(CH_3)_3$. These compounds are called *amines*, and many such are known corresponding to other radicals besides methyl.

The amines have a strong ammoniacal smell which is usually accompanied by a fishy odor. Like ammonia they unite with acids without replacing the hydrogen of the acids. Thus: $NH_2CH_3 + HCl = NH_2CH_3 . HCl$, or methylamine hydrochloride.

The methylamines occur in small quantities in nature. They are all produced by the distillation of wood.

Methylamine, NH_2CH_3, occurs in herring brine. Dimethylamine, $NH(CH_3)_2$, occurs in Peruvian guano. Trimethylamine, $N(CH_3)_3$, occurs quite widely distributed. It is found in various plants, and in the bloom of the pear, wild-cherry, and hawthorn. It also occurs in herring brine. It is now prepared in large quantities by distilling beet root vinasses. It is employed for manufacturing

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[1] The hypothetical radical, NH_2, is often called *amidogen*, and the compounds in which it occurs are termed the *amido*-compounds.

potassium carbonate, just as ammonia is used for making sodium carbonate. The methylamines can be prepared by synthetic processes which are of minor interest to the beginner.

2. *The Cyano-Derivatives.*

220. Cyanogen, CN, and Hydrocyanic Acid, HCN, have been noticed under Arts. 87 and 88. The hydrocarbon radicals unite with hydrocyanic acid to form the cyanides or *Nitrils ; e.g.* methyl cyanide or aceto-nitril, CH_3CN. There is another class of compounds isomeric with the cyanides which have received the distinguishing names of the *Isocyanides* or the *Carbamines ; e.g.* methyl carbamine, CH_3NC.

There is also a hypothetical cyanic acid, CNOH, which gives rise to the cyanates and an isomeric acid yielding the isocyanates, or, as they are frequently called, the *Carbamides* or the *Carbonylamines.*

Ammonium cyanate, NH_4NCO, is of interest, since when heated it undergoes a rearrangement of its atoms, and is converted into *Urea* or *Carbamide.* This substance is a white solid occurring in many animal fluids. It is the first so-called organic compound prepared by synthesis.

There is a remarkable tendency among the cyanogen compounds to polymerize, in consequence of which the number of these compounds is very great. Thus we have $H_3C_3N_3$, a solid called trihydrocyanic acid, a polymer of HCN, hydrocyanic acid. Again, cyanic acid has the polymer, cyanuric acid, $C_3N_3O_3H_3$.

3. *The Nitro-Derivatives.*

221. Nitro-Methane, CH_3NO_2. — The radical NO_2 unites with methyl, ethyl, etc., to form the nitro-compounds.

Nitro-methane is to be had by a variety of reactions, *e.g.* by the action of methyl iodide on silver nitrite : —

$$CH_3I + AgNO_2 = CH_3NO_2 + AgI.$$
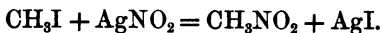
It is a heavy liquid having a characteristic odor. When heated with fuming sulphuric acid, carbon monoxide and *Hydroxylamine* are produced : —

$$CH_3NO_2 = NH_2OH + CO.$$

It acts like a weak acid in uniting with bases to form salts. These salts are violently explosive.

The radical NO can displace hydrogen from the hydrocarbons to form the *Nitroso* and the *Isonitroso* compounds. Fulminic acid, $C_2N_2O_2H_2$, forms, as an example of the isonitroso compounds, $C_2N_2O_2Hg$, which is commonly called fulminating mercury. A mixture of this salt and potassium nitrate is used as the fulminating powder in guncaps. Fulminating mercury is prepared by dissolving mercury in strong nitric acid; then alcohol is added to the solution.

IV. DERIVATIVES WITH SULPHUR, ARSENIC, PHOSPHORUS, ETC.

222. The Mercaptans, Phosphines, Arsines, and Stibines. — With hydrogen sulphide, methyl, ethyl, etc., form a class of compounds called the mercaptans. Methyl mercaptan, CH_3SH, is obtained by treating potassium acid sulphide with methyl iodide : —

$$CH_3I + HKS = CH_3SH + KI.$$
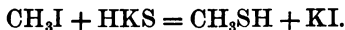
Methyl mercaptan is a liquid of an extremely disagreeable odor. All the mercaptans likewise are disagreeablesmelling compounds.

Both hydrogen atoms in hydrogen sulphide may be replaced by hydrocarbon radicals, thus giving rise to a class of compounds that are comparable to the ethers. Thus we have methyl sulphide, $(CH_3)_2S$; ethyl sulphide, $(C_2H_5)_2S$; etc. These compounds are liquids of disagreeable odors.

By the oxidation of a mercaptan, an acid called a *Sulphonic Acid* is obtained. Methyl sulphonic acid, CH_3HSO_3, and ethyl sulphonic acid, $C_2H_5HSO_3$, will serve as examples. These acids may be regarded as derived from sulphuric acid by replacing one hydroxyl by a radical. Thus, $OHHSO_3$, sulphuric acid, gives CH_3HSO_3, methyl sulphonic acid.

The sulphonic acids form salts with bases. As an example, methyl potassium sulphonate, CH_3KSO_3, may be cited.

Phosphine, PH_3, Arsine, AsH_3, and Stibine, SbH_3, may have one or more of their hydrogens replaced by a hydrocarbon radical to form the *Phosphines*, *Arsines*, and the *Stibines*. The arsine compounds are often called the *Cacodyl* compounds on account of their evil odors.

Sug. Student, write and name the methyl phosphines, arsines, and stibines.

V.   METALLIC DERIVATIVES.

223. A few of the metals combine with the hydrocarbon radicals to form liquid compounds that are mostly volatile. Lead, tin, mercury, aluminum, and zinc are among the metals forming such compounds. Zinc methyl, $Zn(CH_3)_2$, and zinc ethyl, $Zn(C_2H_5)_2$, will serve as examples in which it will appear that the usual laws of valence hold good. There are a few exceptional compounds of little importance.

The list of the methyl compounds considered in the preceding paragraphs is by no means exhaustive; but a sufficient number has been given to show the general characteristics of the methane derivatives. Since the derivatives of the other paraffin hydrocarbons arrange themselves in similar groups, we may next proceed to the ethane derivatives, neglecting all but those ·of the most importance.

ETHANE AND ITS DERIVATIVES.

224. Ethane, C_2H_6. — Ethane is a colorless, odorless gas that burns with a faintly luminous flame. It occurs dissolved in petroleum, and mixed with the gases issuing from gas-wells.

It can be prepared in many ways, one of which has been mentioned. When potassium acetate is subjected to electrolysis in suitable apparatus, ethane is produced together with some other substances that may be removed by washing through bulbs containing potassium hydroxide and sulphuric acid. It is also easily prepared by treating mercuric ethyl with sulphuric acid : —

$$2\,Hg(C_2H_5)_2 + H_2SO_4 = 2\,C_2H_6 + (C_2H_5Hg)_2SO_4.$$
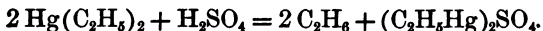
Ethane has no practical application in the arts, and since its halogen derivatives resemble those of methane, we may proceed immediately to the

OXYGEN DERIVATIVES.

225. Ethyl Alcohol, C_2H_5OH or C_2H_6O. — This alcohol is the best known of all the alcohols. It is usually called simply " alcohol " or spirits of wine. It occurs in nature

widely distributed throughout the vegetable kingdom, but in small quantities.

Owing to the enormous quantities consumed in different ways its artificial production is now one of the industries of the age. It can be built up synthetically, but for commerce it is always produced by the action of ferments on such substances as starch and the sugars.

EXP. 94. Place in a large bottle about 1^1 of a dilute solution of grape sugar or of molasses. Add a little baker's yeast and fit a cork carrying a bent delivery-tube which dips down into a test-tube containing a solution of calcium hydroxide. Place the bottle in a moderately warm place and allow it
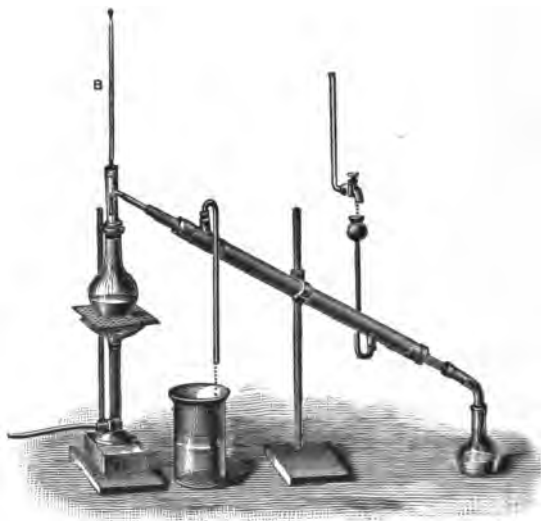
FIG. 35.

to stand until carbon dioxide ceases to come off (note the calcium hydroxide solution from time to time). When fermentation has ceased, place the contents of the bottle in the distilling-flask of an apparatus arranged as in Fig. 35. Distil

until about 100^{cc} of the distillate is collected in the receiver. The reaction for cane sugar is : —

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2.$$

Test the distillate for alcohol by the odor and by the iodoform reaction thus : Warm a small portion of the liquid in a test-tube, and add a few crystals of iodine. Then add sufficient potassium hydroxide to decolorize the solution. Now allow the contents of the tube to cool, when yellow crystals of iodoform will be deposited.

In order to obtain the alcohol in a state of greater purity, the distillate may be treated by a process termed *Fractional Distillation.*

Exp. 95. Place the distillate just obtained in a smaller flask and connect it to the same condensing apparatus used before. Maintain a temperature by means of the thermometer B of about 80° to 90°, until half the liquid has distilled over. Reject what remains in the flask, return the distillate to the flask, and distil off about one-half once more. Now note that the distillate is stronger in alcohol than any portion previously obtained.

This process is much employed in separating liquids which boil at different temperatures.

In the commercial preparation of alcohol, grains, fruits, potatoes, and rice are employed. After the substance employed has fermented, the alcohol is separated, to a great extent, from its accompanying impurities in its water solution in huge stills which are so arranged that the water is mostly condensed and allowed to flow back while the alcoholic vapors pass on and are condensed in other portions of the apparatus. But the commercial alcohol thus obtained is not pure. It contains some water and a mixture of the higher alcohols which is termed fusel oil. These can be further removed by fractionation and by filtering

through boneblack. Some water still remains, which is mostly removed by treatment with quicklime or other hygroscopic agents, after which it is again distilled. Finally the insignificant portion of water that still remains is removed by means of metallic sodium, and a final distillation. In this way *Absolute Alcohol* is prepared.

Ethyl alcohol is the intoxicating principle found in such beverages as whiskey, brandy, gin, rum, wine, beer, and cider. These substances vary in their alcoholic content and in other respects. While there is no uniformity, the first four contain from 25 to 50 or even 55 per cent, and the last three from 5 to 20 per cent of alcohol. The differences of taste and odor are due to the materials from which they are prepared. It seems that each substance gives rise to certain peculiar ethereal essences and other ingredients which imparts to the liquor manufactured from it a distinctive flavor.

Ex. State from what substances each of the beverages just mentioned is produced.

Pure alcohol is a limpid liquid of a pleasant and slightly ethereal odor. It mixes with water with great avidity in all proportions. It boils at 78.3° and has been frozen at −130.5°.

Ex. Name the uses of commercial alcohol.

It has been stated that, corresponding to each primary hydrocarbon, there is, in theory at least, a primary alcohol. A list of these primary alcohols, so far as known, for the paraffin series, is given in Art. 228.

But if we begin with propyl alcohol, C_3H_8O, there are some isomeric alcohols, called *secondary* alcohols, in addition to the primary alcohols, for some of the remaining paraffin hydrocarbons. These isomers may be considered

as derived from methyl alcohol by the replacement of two hydrogens by an alcohol radical. Thus, if we represent

methyl alcohol by $C\begin{cases} H \\ H \\ H \\ OH \end{cases}$, we can represent secondary

propyl alcohol by $C\begin{cases} CH_3 \\ CH_3 \\ H \\ OH \end{cases}$. Also, if we call methyl alco-

hol by the name "carbinol" as has been proposed, we can name secondary propyl alcohol "dimethyl carbinol." The following list gives the secondary alcohols of the paraffins : —

LIST OF SECONDARY ALCOHOLS.

Boiling-point.

Secondary propyl alcohol
or
Dimethyl carbinol
$\Big\}$ $C_3H_8O = C\begin{cases} CH_3 \\ CH_3 \\ H \\ OH \end{cases}$ . . 84°.

Secondary butyl alcohol
or
Methyl-ethyl-carbinol
$\Big\}$ $C_4H_{10}O = C\begin{cases} CH_3 \\ C_2H_5 \\ H \\ OH \end{cases}$ . . 97°.

Secondary amyl alcohol
or
Methyl-propyl-carbinol
$\Big\}$ $C_5H_{12}O = C\begin{cases} CH_3 \\ C_3H_7 \\ H \\ OH \end{cases}$ . . 108°.

Secondary hexyl alcohol
or
Methyl-butyl-carbinol
$\Big\}$ $C_6H_{14}O = C\begin{cases} CH_3 \\ C_4H_9 \\ H \\ OH \end{cases}$ . . 136°.

Secondary octyl alcohol
or
Methyl-hexyl-carbinol
$\Big\}$ $C_8H_{18}O = C\begin{cases} CH_3 \\ C_6H_{13} \\ H \\ OH \end{cases}$ . . 181°.

Beginning with butyl alcohol there is, in addition to the two classes of alcohols already described, a third class, called *tertiary* alcohols, made by replacing three hydrogens from methyl alcohol, with alcohol radicals.

LIST OF TERTIARY ALCOHOLS.

Boiling-point.

$$\left.\begin{array}{c}\text{Tertiary\ \ butyl\ \ alcohol}\\ \text{or}\\ \text{Trimethyl-carbinol}\end{array}\right\} C_4H_{10}O = C \left\{ \begin{array}{l}(CH_3)_3\\ OH\end{array}\right. \quad 82°.$$

$$\left.\begin{array}{c}\text{Tertiary\ \ amyl\ \ alcohol}\\ \text{or}\\ \text{Dimethyl-ethyl-carbinol}\end{array}\right\} C_5H_{12}O = C \left\{ \begin{array}{l}(CH_3)_2\\ C_2H_5 .\\ OH\end{array}\right. \quad 100°.$$

$$\left.\begin{array}{c}\text{Tertiary\ hexyl\ alcohol}\\ \text{or}\\ \text{Dimethyl-propyl-carbinol}\end{array}\right\} C_6H_{14}O = C \left\{ \begin{array}{l}(CH_3)_2\\ C_3H_7\\ OH\end{array}\right. \quad 120°.$$

$$\left.\begin{array}{c}\text{Methyl-diethyl\ \ methane}\\ \text{or}\\ \text{Methyl-diethyl-carbinol}\end{array}\right\} C_6H_{14}O = C \left\{ \begin{array}{l}CH_3\\ (C_2H_5)_2 .\\ OH\end{array}\right. \quad 115°.$$

$$\left.\begin{array}{c}\text{Tertiary\ \ heptyl\ \ alcohol}\\ \text{or}\\ \text{Triethyl\ \ carbinol}\end{array}\right\} C_7H_{16}O = C \left\{ \begin{array}{l}(C_2H_5)_3\\ OH\end{array}\right. \quad —$$

$$\left.\begin{array}{c}\text{Tertiary\ \ octyl\ \ alcohol}\\ \text{or}\\ \text{Diethyl-propyl-carbinol}\end{array}\right\} C_8H_{18}O = C \left\{ \begin{array}{l}(C_2H_5)_2\\ C_3H_7\\ OH\end{array}\right. \quad —$$

226. Ethyl Ether, $(C_2H_5)_2O$. — This is commonly known simply as "ether." It is the best known of any of the substances in the class to which it belongs. Ether is prepared for commerce by the action of sulphuric acid on ethyl alcohol.

Exp. 96. Fit a flask with a cork containing three holes. In one hole place a delivery-tube, in the second a thermometer,

and in the third a funnel-tube. Place in the flask a mixture of alcohol (90 per cent), five parts, and concentrated sulphuric acid, nine parts. Insert the cork, allowing the thermometer and the funnel-tube to dip below the liquid. Now join the delivery-tube to a condenser, and heat the mixture up to the boiling-point, which should be about 140°. Allow alcohol to enter the funnel-tube, drop by drop, while the liquid is boiling. When about 25^{cc} of distillate have collected in the condenser, the operation may be brought to a close. Place the distillate in a large test-tube, add water, and shake. Note the layer of ether which collects above the water. Note its odor, and be careful not to bring it near a flame. Pour a few drops on the hand, and allow it to evaporate.

The reactions take place in two stages. At first ethyl sulphuric acid is formed : —

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$
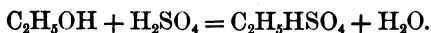
Then another molecule of alcohol and this ethyl sulphuric acid react to form ether and sulphuric acid : —

$$C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4.$$
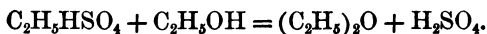
This sulphuric acid is now ready to act upon another molecule of alcohol to form ethyl sulphuric acid again, which in turn may once more react with another molecule of alcohol to form more ether. Thus the process becomes continuous, and, in theory, a small quantity of sulphuric acid may form an unlimited amount of ether ; but in practice, the acid after a while becomes too dilute, and the reaction ceases.

Ether is an extremely mobile, inflammable liquid, which boils at 34.9°, and at 0° has a specific gravity of 0.73568.

Ether has many uses. In the laboratory and in the arts and manufactures it is used as a solvent. It is also used in manufacturing ice ; and in medicine it is used as an

anæsthetic. Its action upon the system is similar to that of laughing-gas.

227. Ethyl Aldehyde, C_2H_4O. — This substance is also known as acetaldehyde, since by further oxidation it . passes into acetic acid. It is a liquid which has a peculiar ethereal, but suffocating odor. When inhaled in quantities, it acts violently upon the system.

Exp. 97. To a solution of potassium bichromate, in a test-tube, add sulphuric acid until the solution becomes dark red. Then add a small quantity of alcohol. Note the odor, which is that of "aldehyde," as the ethyl aldehyde is commonly called.

Aldehyde is used in the arts for the preparation of aldehyde green, one of the so-called aniline colors. Commercial aldehyde is a by-product obtained in the manufacture of alcohol.

Aldehyde is capable of yielding substitution products, one of which is known as *Chloral*, C_2HCl_3O. Chloral may be regarded as aldehyde in which three atoms of hydrogen have been displaced by chlorine. It is a colorless liquid, which unites with water to form the valuable medicine, *Chloral Hydrate*, $C_2HCl_3O.H_2O$. In practice, chloral is obtained by treating absolute alcohol with chlorine for six or eight weeks, after which the solution is kept in contact with sulphuric acid until the chloral separates out. After purification, the requisite amount of water is added to produce the hydrate. This hydrate is used as an anæsthetic and an hypnotic.

228. Acetic Acid, $C_2H_4O_2$ or $HC_2H_3O_2$. — Acetic acid is one of the most valuable of the organic acids. In weak and impure solutions it is known as *Vinegar*. When fruit juices, such as those of the apple and grape, are kept at

the proper temperature, alcoholic fermentation first sets in. The weak solution of alcohol thus obtained, under the proper conditions undergoes another kind of fermentation, known as acetous fermentation. This latter action is due to the presence of a microscopic organism, *Mycoderma aceti*, commonly called "mother of vinegar." Hence it appears that the acetic acid of vinegar is really an oxidation product of alcohol. Vinegar is now prepared, on the large scale, by allowing weak alcoholic solutions to trickle slowly through wooden casks filled with shavings. The rapidity of the action is greater when some mother of vinegar is present.

FIG. 36.

The source of the pure acetic acid used in the laboratory is the crude acetic or pyroligneous acid obtained in distilling wood. A metallic salt of acetic acid is first prepared and purified. Then this salt is treated with sulphuric acid, and distilled. The acetic acid thus obtained is freed from water by distillation, thus giving *Glacial Acetic Acid*.

Acetic acid is a stable monobasic acid which yields a well-known series of salts, — the acetates. It also yields a series of substitution products. Thus acetyl chloride, C_2H_3OCl, is used as a reagent in the laboratory.

When an acetate is subjected to distillation, a substance known as *Acetone*, C_3H_6O, is obtained : —

$$Ca(C_2H_3O_2)_2 = C_3H_6O + CaCO_3.$$
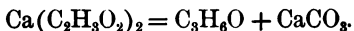
Acetone is a substance closely allied to aldehyde, and is a representative of a class of compounds called the *Ketones*.

We have now studied methyl and ethyl alcohols, and formic and acetic acids. These are the most important substances of their classes, derived from the paraffins, and space forbids notice of the less important compounds of a similar nature. But the following table gives a list of the primary alcohols of the methane series, together with their corresponding acids : —

PRIMARY ALCOHOLS, General formula, $C_nH_{2n+2}O$,			yield	FATTY ACIDS,[1] General formula, $C_nH_{2n}O_2$.			
Name.	**Formula.**	**Boiling-Point.**		**Name.**	**Formula.**	**Boiling-Point.**	**Melting-Point.**
Methyl . . .	$C\ H_4\ O$	66°C.		Formic . . .	$C\ H_2\ O_2$	100°	1°
Ethyl	$C_2\ H_6\ O$	78°.4		Acetic . . .	$C_2\ H_4\ O_2$	118°	17°
Propyl . . .	$C_3\ H_8\ O$	96°		Propionic .	$C_3\ H_6\ O_2$	140°	−20°[3]
Butyl	$C_4\ H_{10}O$	109°		Butyric . .	$C_4\ H_8\ O_2$	162°	—
Amyl	$C_5\ H_{12}O$	132°		Valeric . . .	$C_5\ H_{10}O_2$	174°	—
Hexyl	$C_6\ H_{14}O$	150°		Caproic . .	$C_6\ H_{12}O_2$	199°	5°
Heptyl . . .	$C_7\ H_{16}O$	164°		Œnanthylic	$C_7\ H_{14}O_2$	219°	—
Octyl	$C_8\ H_{18}O$	196°		Caprylic . .	$C_8\ H_{16}O_2$	236°	16°
Nonyl	$C_9\ H_{20}O$	—		Pelargonic .	$C_9\ H_{18}O_2$	254°	18°
Decatyl . . .	$C_{10}H_{22}O$	212°		Capric . . .	$C_{10}H_{20}O_2$	—	30°
Hendecatyl .	$C_{11}H_{24}O$	—		Lauric . . .	$C_{12}H_{24}O_2$	—	43.6°
Dodecatyl .	$C_{12}H_{26}O$	—		Myristic . .	$C_{14}H_{28}O_2$	—	53.8°
Cetyl	$C_{16}H_{34}O$	49.5°[2]		Palmitic . .	$C_{16}H_{32}O_2$	—	62°
——	—	—		Margaric . .	$C_{17}H_{34}'O_2$	—	—
——	—	—		Stearic . . .	$C_{18}H_{36}O_2$	—	69.2°
——	—	—		Arachidic .	$C_{20}H_{40}O_2$	—	75°
——	—	—		Behenic . .	$C_{22}H_{44}O_2$	—	76°
——	—	—		Hyænic . .	$C_{25}H_{50}O_2$	—	77°
Ceryl	$C_{27}H_{56}O$	79°[2]		Cerotic . . .	$C_{27}H_{54}O_2$	—	78°
Myricyl . . .	$C_{30}H_{62}O$	85°[2]		Melissic . .	$C_{30}H_{60}O_2$	—	88°

[1] So called because some of them occur in fats.
[2] Melting-points.   [3] Below.

Some of the acids given in the foregoing table occur in well-known substances. Butyric acid occurs in butter. Palmitic acid occurs in many fatty compounds, such as palm oil, olive oil, and cocoanut oil. Stearic acid occurs in such solid fats as mutton and beef tallow. These acids are combined in their natural fats, as palmatin and stearin, with an alcohol of the formula, $C_3H_8O_3$, commonly called glycerine. Melissic acid occurs in beeswax.

229. Soap. — EXP. 98. Melt 35^g of cocoanut or cotton-seed oil with 18^g of good tallow in a large evaporating-dish or tin basin. Then add a solution of 16.5^g of potassium hydroxide dissolved in 40^{cc} of water. Heat the substances carefully, when a chemical reaction termed *Saponification* will soon ensue. The heat must now be quickly removed, to prevent boiling over. When the action ceases, apply heat again, and boil gently for about fifteen minutes. Now add about 10^g of common salt, and cook for thirty minutes.

Separate the soap as completely as possible from any "spent lye" that may be in the bottom of the dish, and place the soap in a shallow tin or pasteboard box to cool. Test the properties of the soap for cleansing and for making a lather.

When natural fats consisting of palmatin, stearin, and olein — a compound found in many liquid oils, and containing oleic acid, $C_{18}H_{34}O_2$ — are heated with an alkali, glycerine is set free, and the fatty acids unite with the metal of the alkali to form salts. These salts constitute what we call soap.

Soaps may be distinguished as hard and soft soaps, depending upon the fats and the alkalies which enter into their composition. The soft soaps usually contain cheap oils, such as lard, fish oil, and house scraps (usually called soap grease).

Frequently wood ashes are leached and the potash lye thus obtained is boiled with soap grease, to make soft soap. Cocoanut oil, olive oil, and tallow make the best hard soaps. They are usually combined with caustic soda.

When soap is brought in contact with hard water, a curd is formed which consists of insoluble calcium palmate, stearate, and oleate.

230. Ethyl Nitrite, $C_2H_5NO_2$. — It is not necessary to notice the remaining derivatives of ethane. But there is one among the nitrogen derivatives, ethyl nitrite, that is an article of commerce. This substance may be obtained by adding potassium nitrite to ethyl sulphuric acid : —

$$C_2H_5HSO_4 + KNO_2 = C_2H_5NO_2 + HKSO_4.$$
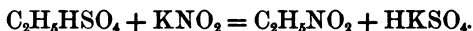
A solution of ethyl nitrite in alcohol is sold in drug stores as sweet spirit of nitre, or *spiritus ætheris nitrosi*. It is used as a mild irritant; its action on the kidneys is also well known.

CHAPTER XVII.

A FEW DERIVATIVES OF THE ETHYLENE SERIES AND OF THE ACETYLENE SERIES.

I. THE OLEFINE DERIVATIVES.

231. Ethylene, C_2H_4. — This important gas has already been mentioned as forming the most important constitu- . ent of illuminating gas produced by the distillation of coal. In this connection it is of interest since it is the lowest member of the olefine series. The members of this series belong to that class of compounds called unsaturated compounds. They form addition products in which they act like bivalent radicals. The alcohols, often called *Glycols*, and the acids are the most important of the olefine derivatives. The alcohols of this series yield two classes of acids. In the first class, the *Lactic Acid Series*, the acids are monobasic, and they are derived from their corresponding alcohols by displacing two atoms of hydrogen and taking up one atom of oxygen. In the second, or *Oxalic Acid Series*, the acids are dibasic and are derived from their corresponding alcohols by the displacement of four atoms of hydrogen and the addition of two atoms of oxygen. Among these acids are found some of the best known of the organic acids. They occur quite widely distributed in nature. They form well-defined series of salts with the metals, some of which are of frequent and extended use.

The following table will show the relations between the olefine alcohols and their acids : —

Hydro-carbons.	Alcohols, or Glycols.	Acids (Monobasic).	Acids (Dibasic).
C_2H_4	Ethylene, $C_2H_4(OH)_2$	Glycollic, $C_2H_4O_3$	Oxalic, $C_2H_2O_4$
C_3H_6	Propylene, $C_3H_6(OH)_2$	Lactic, $C_3H_6O_3$	Malonic, $C_3H_4O_4$
C_4H_8	Butylene, $C_4H_8(OH)_2$	Butylactic, $C_4H_8O_3$	Succinic, $C_4H_6O_4$
C_5H_{10}	Amylene, $C_5H_{10}(OH)_2$	Valerolactic, $C_5H_{10}O_3$	Pyrotartaric, $C_5H_8O_4$
C_6H_{12}	Hexylene, $C_6H_{12}(OH)_2$	Leucic, $C_6H_{12}O_3$	Adipic, $C_6H_{10}O_4$

232. Lactic Acid, $C_3H_6O_3$. — Lactic acid occurs in sour milk, where it is produced by the action of a lactic acid ferment, *Penicillum glaucum*, on the sugar of milk. It also occurs in the juices of vegetables that have turned sour. It has not been prepared in the anhydrous condition. It forms a series of salts with the metals that are almost all uncrystallizable and very deliquescent. Lactic acid has two isomers.

233. Oxalic Acid, $C_2H_2O_4$. — This acid occurs as the acid potassium salt in plants belonging to the species known as Oxalis and in other plants.

It can be prepared in a variety of ways, but it is now prepared for commerce by heating pine sawdust with caustic potash. Usually a mixture of caustic soda and caustic potash is employed instead of the caustic potash alone. The fused mass is treated with water, when all but the sodium oxalate dissolves. This salt is ignited and then treated with lime-water, whereupon insoluble calcium oxalate and caustic soda are obtained. From the calcium oxalate, oxalic acid is liberated by means of sulphuric acid, which gives insoluble calcium sulphate and free oxalic acid. From the acid thus obtained in solution, crystals of oxalic acid are secured by concentration and crystalli-

zation. The caustic alkalies are regained and used to act upon more sawdust.

Oxalic acid is readily soluble in water and in alcohol, and upon the system it acts as a poison when taken in large doses. It forms, with the metals, a series of salts, the oxalates, that are used in a variety of ways. Both the acid and its salts possess bleaching properties, and some of the salts serve as useful reagents in the laboratory.

234. Succinic Acid, $C_4H_6O_4$. — Succinic acid occurs in amber in certain lignites and in fossil wood. It also occurs in such plants as lettuce and wormwood. It is also one of the products of alcoholic and acetic acid fermentation.

Commercial succinic acid is prepared by distilling amber and by the fermentation of calcium malate and of tartaric acid.

235. Malic Acid, $C_4H_6O_5$. — This acid occurs in the juices of fruits, like apples, pears, gooseberries, raspberries, and currants. It can best be prepared from mountain-ash berries or from the stems and leaves of garden rhubarb. The juice is expressed and treated with milk of lime, when insoluble calcium malate is obtained. This salt is purified, and then decomposed by means of sulphuric acid. This gives insoluble calcium sulphate and malic acid.

By comparing the formula of this acid with that of succinic acid, it will appear that malic acid simply has one atom more of oxygen than succinic acid. Hence malic acid is often called *oxy-succinic* acid.

236. Tartaric Acid, $C_4H_6O_6$. — This acid occurs widely distributed in nature. It occurs both in the free state

and in the form of salts in many fruits along with malic acid. Hydrogen potassium tartrate occurs plentifully in the juice of grapes, from which it is deposited along with the calcium salt during the fermentation of grape juice in the manufacture of wine. The crude salts thus obtained are called " Argols " and are employed in assaying.

Tartaric acid crystallizes in large transparent prisms, soluble in alcohol and in water. This acid finds many uses in the arts, while the hydrogen potassium salt, $KHC_4H_4O_6$, often called cream of tartar, is extensively employed in the manufacture of baking-powder. For this purpose this salt is mixed with acid sodium carbonate, and a certain quantity of starch is added as a "filler" to prevent chemical reaction between the other ingredients while in a dry state. This tartrate finds other uses, as in medicine, in silvering, in soldering, and in dyeing. Tartar emetic has been mentioned under antimony, Art. 137.

Tartaric acid has two atoms of oxygen more than succinic acid, whence the name *Dioxy-succinic* acid which it often bears. The acids of the olefines each have two or more isomers which are sometimes distinguished by their action on polarized light. One may rotate the plane of polarization to the right, another to the left, while perhaps a third will be optically inactive.

237. Citric Acid. — This acid belongs to a class of compounds called hydroxy acids, since it contains a hydroxyl group, as appears from the rational formula, $C_3H_3(OH)(CO_2H)_3$. It is a tribasic acid, yielding both acid and normal salts.

It occurs widely distributed in nature like malic and tartaric acids. It is obtained for commerce from lemon juice.

The juice is allowed to ferment, lime is added, and the calcium citrate thus obtained is then purified, and afterwards treated with sulphuric acid.

It is also found in the orange, cranberry, and whortleberry. With about an equal quantity of malic acid it occurs in the currant, gooseberry, strawberry, cherry, and raspberry, and berries of the mountain-ash.

This acid is much used in preparing lemonade and other cooling drinks. It also is used in medicine, in calico-printing, and in dyeing. Of its salts, magnesium citrate, $Mg_3(C_6H_5O_7)_2 + 14 H_2O$, made by dissolving magnesia, MgO, in citric acid, is used in medicine as a mild purgative. Effervescing citrate of magnesia is made by adding to this salt citric acid, acid sodium carbonate, and sugar. The whole is then moistened with alcohol and afterwards dried.

238. Glycerine, Glycerol, or Propenyl Alcohol, $C_3H_5(OH)_3$. — Glycerine, as will appear from its formula, is a triad alcohol containing three hydroxyls. This is the best-known compound of its class. In comparing with propylene, C_3H_6, it appears that not only are the two combining equivalents of propylene satisfied with hydroxyls, but also one hydrogen is replaced by a hydroxyl.

Glycerine, as already mentioned, occurs in most of the fats from which it can be separated by saponification. It can also be isolated by treating the natural fats with superheated steam; and it is in this way that a larger part of the glycerine of commerce is prepared.

Glycerine is a syrupy, odorless liquid of a sweetish, pleasant taste. It is readily soluble in alcohol and in water, but insoluble in ether and chloroform. It is much used in pharmaceutical preparations, for manufacturing

copying-ink, for "improving" liquors, and, owing to the ease of its digestibility, for a food.

But perhaps the largest consumption of glycerine is for the manufacture of the powerful, high-grade, explosive *nitro-glycerine*, $C_3H_5(NO_2)_3$. This compound is made by treating one part of glycerine with a mixture consisting of four parts of sulphuric acid and one part of nitric acid, at a low temperature. The nitro-glycerine separates out as an oily liquid, and it must be carefully freed from acids to prevent its decomposition, which is frequently accompanied by terrific explosions. But at its best the liquid is not safe to handle. Consequently it is now mostly used in the form of *dynamite* or *giant powder*. These substances are prepared by allowing absorbent substances like Kieselguhr, a siliceous kind of earth, to take up the liquid. In this form nitro-glycerine is much used in blasting. It is usually exploded by percussion.

239. Oleic Acid, $C_{18}H_{34}O_2$. — This acid occurs in most of the liquid fats and many solid fats combined with glycerine. It is obtained in large quantities as a by-product in manufacturing stearin candles. A crude form of this acid containing other fatty acids may be had by dissolving castile soap in water, and then treating the solution with hydrochloric acid.

II. ACETYLENE DERIVATIVES.

240. Linoleic Acid, $C_{16}H_{28}O_{24}$. — Acetylene has been mentioned in Art. 82. Of the derivatives belonging to the acetylene series we shall notice but one or two.

Linoleic acid occurs combined with glycerine as trilinolein in linseed oil. It is to this compound that linseed

(flaxseed) oil owes its value as an ingredient of paints. When a thin layer of linseed oil is exposed to the air, oxygen is taken up, and the glycerine is oxidized, leaving a gummy mass behind which is little acted upon by heat or moisture. For the same reasons linseed oil is much used in the manufacture of varnishes.

241. Mannite, or Mannitol, $C_6H_8(OH)_6$. — Just as glycerine is a triad alcohol, so is mannite a hexad alcohol. This substance occurs in manna, the dried sap of certain species of ash, as *Fraxinus ornus* and *F. rotundifolia*. It also occurs in many other forms of vegetation, as in the roots of celery, in the sugar-cane, in olives, and in many fungus-like plants.

The manna mentioned in the Bible contained no mannite, but instead a kind of sugar. It was probably the dried sap of a species of Tamarix. The manna mentioned as falling from heaven may have been a kind of lichen, *Spærothallia esculenta*, which is carried about by the winds.

There is an isomer of mannite which is called *Dulcite*. Both these substances possess a sweetish taste, and are more closely related to the carbohydrates of the next chapter than to any other class of compounds.

CHAPTER XVIII.

THE CARBOHYDRATES.

242. Carbohydrates is a term applied to a class of carbon compounds containing hydrogen and oxygen in the same proportion as found in water. These substances seem to be closely allied to the hexad alcohols, but the exact relations are not very clearly defined.

For convenience of consideration the carbohydrates may be divided into three classes : —

1. The *Sucroses*, $C_{12}H_{22}O_{11}$, embracing cane sugar, milk sugar, maltose, etc.

2. The *Glucoses*, $C_6H_{12}O_6$, embracing grape sugar, levulose, etc.

3. The *Amyloses*, $(C_6H_{10}O_5)_n$,[1] including starch, dextrine, gums, cellulose, etc.

These compounds are of the greatest importance. They occur widely distributed throughout the vegetable kingdom, and they play an important part in the nourishment and growth of both plants and animals. The sucroses and glucoses are sweet to the taste and freely soluble in water. The amyloses are generally tasteless and insoluble in water. The first two classes are remarkable for their power of rotating the plane of polarized light. Cane sugar, milk sugar, maltose, and grape sugar rotate the plane to the right ($+$), while levulose rotates it to the left ($-$).

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[1] This formula indicates that the molecular formulas are not exactly determined.

Again, many of these compounds possess the property of reducing solutions of cupric salts to cuprous oxide. Upon the two properties last named the methods employed for the quantitative determination of the sugars are based. Thus cane sugar is determined by its dextro-rotary power, specially constructed apparatus being employed, while glucose is estimated by its reducing effect on Fehling's solution, an alkaline solution of copper sulphate, Rochelle salts, and sodium hydroxide.

THE SUCROSES.

243. Sucrose, or Cane Sugar, $C_{12}H_{22}O_{11}$. — This is the best known of all the sugars. It is of wide distribution, and is prepared for commerce in enormous quantities. The principal sources of cane sugar are the sugar beet, the sugar-cane, the sugar maple, and sorghum. Until recently the sugar-cane furnished the larger part of the sugar of commerce; but recent estimates now accredit that honor to the sugar beet. The sugar beet contains from eight to twenty per cent of cane sugar and the sugar-cane from fourteen to twenty. In exceptional cases the percentages for both have been known to exceed twenty per cent.

There have been many processes employed in manufacturing sugar. The simplest of these is the one employed in making maple sugar. An incision is made in the tree, and just beneath is fastened a spile or spout which carries the sap into a trough or bucket placed at the foot of the tree. At intervals the sap is collected and carried to large kettles or pans that are frequently placed in the sugar forest at some convenient location. These kettles are often placed in the open air, and are heated by means of direct fires. Here the sap is evaporated, and any scum that rises

is simply skimmed off. When the sap reaches a syrupy consistence, it is removed from the large kettles, and the "sugaring off" is completed in smaller kettles, very frequently on the kitchen stove. In this latter process the concentration is carried on till the sugar will grain on cooling, when it is placed in pans or tins and allowed to cool. It is now ready for market.

Of late many improvements have been introduced into the manufacture of sugar from sugar beets and sugar-cane. That known as the "diffusion process" is by all means the best. In this process the canes or beets are first cut into thin slices, or sometimes in the case of beets they are torn into shreds. Now by the judicious application of hot water the sugar diffuses through the cell walls of the plants, leaving behind most of the uncrystallizable impurities. In order to accomplish this end, a series of from twelve to sixteen boiler-iron cylinders or "cells" are arranged in a circle to form what is termed a "battery."

These cells are first filled with the chips, and then a charge of hot water and steam is introduced into No. 1. From here the water is next forced into No. 2, and then into No. 3, and so on around. When the last cell is reached the water has taken up sugar from every cell until it is now a somewhat concentrated sugar solution.

It will readily be understood that the chips in the first cell where the water was pure have lost more sugar than the chips in any of the succeeding cells; also that as the water passed along from cell to cell it gradually took less and less sugar, so that the chips in the last cell were exhausted least of all. From the last cell the concentrated solution is run into a large liming-tank, and a fresh charge

of water is started in again at No. 1 and passed around as before.

Other charges of water are then introduced into No. 1 and passed around until the chips in that cell are exhausted. Then these chips are removed and fresh ones are introduced. Now the next charge of fresh water is started at No. 2, and finally taken out at No. 1. Then fresh chips are placed in No. 2, and the next charge of water is started at No. 3 and taken out at No. 2; and thus the process is continued.

When the liming-tank is filled, it is heated, and lime is added to remove impurities. From this tank the juice is passed into another, where the excess of lime is removed by means of carbon dioxide. If necessary, the juice is next filtered through boneblack filters, from which it is passed into vacuum pans, where it is concentrated until the crystallizing-point is reached. The crystals are removed and dried in centrifugal driers. By further concentration a second and even a third crop of crystals may be obtained, when nothing is left excepting uncrystallizable molasses. The molasses from beet sugar is much used for manufacturing alcohol.

Raw sugars from the cane and from beets are usually sent to the refiners, where the remaining impurities are removed, and the sugar worked up in a variety of ways ready for the market.

France and Germany now produce most of the beet sugars of the world. This industry now bids fair to become established in the United States.

Cane-sugar crystals obtained by slow evaporation are large and transparent, but when the crystals are formed rapidly, they are small, striated, and nearly opaque. Water at 45° dissolves nearly two and a half times its weight of

cane sugar. When fused at about 175° for some time, sugar is changed into a mixture of levulosan and dextrose : —

$$C_{12}H_{22}O_{11} = C_6H_{10}O_5 + C_6H_{12}O_6.$$

When heated to higher temperatures a substance called *Caramel* is produced. When submitted to still higher temperatures, or when treated with concentrated sulphuric acid, sugar is decomposed, oxygen and hydrogen in the proportions found in water are removed, and carbon is left behind.

Exp. 99. Dissolve 2^g or 3^g of sugar in about the same quantity of water, and while the solution is warm slowly add concentrated sulphuric acid. Note the remaining carbon.

When sugar in water solution is strongly heated or exposed to the action of dilute acids, or of certain other reagents, it is changed into "invert sugar," which is lævorotary, and which consists of a mixture of equal parts of levulose and dextrose : —

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$
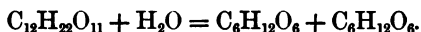
In alcoholic fermentation the ferment first changes the sugar into invert sugar, after which the conversion into alcohol proceeds by the further action of the ferment on the invert sugar. Cane sugar of itself is not fermentable.

244. Milk Sugar, Lactose, $C_{12}H_{22}O_{11}$. — Milk sugar is an isomer of cane sugar, which occurs in the milk of the Mammalia, and of which it constitutes about four per cent. This sugar is said to occur in but one plant, a tree, *Sapota achras*, a native of the West Indies.

Commercial milk sugar is prepared from milk whey, which is simply concentrated and allowed to stand in a cool place until the sugar separates out in crystals. Some-

times the crystallization is aided by suspending strings in the whey. As found in commerce, milk sugar usually consists of elongated crystalline masses containing one equivalent of water. It is hard and gritty, and is not very sweet to the taste. It is employed in medicine.

When the sugar in milk ferments, it yields lactic acid and alcohol. The lactic acid coagulates the albumen of the milk, and thus causes the milk to thicken.

Maltose is also an isomer of cane sugar, which is prepared by the action of malt on starch. There are several other isomers of cane sugar which are of less importance.

THE GLUCOSES.

245. Grape Sugar, Dextrose, or Glucose, $C_6H_{12}O_6$. — Grape sugar occurs widely distributed in plants along with equal parts of levulose, the two forming invert sugar. Some cane sugar is usually present at the same time. Grape sugar also occurs in honey, but it is most plentiful in the sweet juices of ripe fruits such as grapes, cherries, etc.

This sugar is called dextrose, owing to its dextro-rotary action on polarized light.

Under the name of *Glucose* grape sugar is now manufactured in enormous quantities by heating starch with water containing from one to two per cent of sulphuric acid.

Exp. 100. To 100^{cc} of water in a flask add 1^{cc} of sulphuric acid, and boil. Slowly add to the contents of the flask, without checking the boiling, 10^g of starch which have been made into a paste with water. Boil for three hours. Then add powdered chalk or marble until the acid is completely neutralized, and then filter. Finally evaporate the filtrate to a thick syrup, and then set it away in a cool place. Note the taste, and from time to time examine the solution for crystals of glucose.

The preceding experiment illustrates in a general way the process employed in manufacturing glucose. Glucose is now extensively used in the manufacture of candy and syrups and for the adulteration of cane sugar. It is cheaper than cane sugar, and is not so sweet. Unless properly purified it contains some substances which act upon the system like the pernicious fusel oil found in impure alcoholic liquors.

Exp. 101. Test samples of sugar, candy, and syrups for glucose, thus: First prepare one-half litre of Fehling's solution as follows: Dissolve 17.32^g pure copper sulphate in a small quantity of water, and then add 100^g of Rochelle salts (sodium potassium tartrate). Then add about 300^{cc} of a solution of sodium hydroxide of a specific gravity 1.12. Then dilute to one-half litre by adding pure water.

Now place about 10^{cc} of the clear blue solution thus prepared in a large test-tube, and boil. While still boiling add a few drops of a water solution of the substance to be tested, and continue the boiling for a short time. Then add a few drops more of the same solution, and boil as before. If the Fehling's solution loses color, add more of the substance to be tested, and boil. Continue this process until the color is destroyed. Now allow the solution to stand a short time, and if a reddish precipitate of cuprous oxide collects in the tube, glucose is present. Cane sugar has no reducing effect on the copper solution.

Levulose, which has already been mentioned several times, occurs with dextrose in fruits, etc. It it a lævo-rotary isomer of dextrose that does not crystallize. It is nearly as sweet as cane sugar.

THE AMYLOSES.

246. Starch, or Amylum, $(C_6H_{10}O_5)_n$. — Starch occurs in nearly every part of most growing plants, and especially of

those plants containing chlorophyll. It is formed from the protoplasm which the chlorophyll cells contain. But the largest deposits are to be found in seeds, grains, tubers, bulbs, and piths, where the starch is stored away to furnish material for the next season's growth. Some biennial and perennial plants make deposits of starch in their thickened leaves for the same purpose.

Exp. 102. Agitate about 100^g of wheat bran with sufficient water to form a thin paste. Filter through a linen cloth, using pressure if necessary. Allow the filtrate to stand for some time. Test the white sediment that is deposited for starch, by moistening a part of it with a dilute solution of iodine in potassium iodide solution. If starch be present, it will turn blue. Moisten a second portion of the sediment with a dilute solution of potassium iodide, and then examine it with a microscope magnifying from 200 to 300 diameters. Similarly prepare and test starch from corn and potatoes. Also examine the pith of growing twigs of trees for starch.

Starch is prepared for commerce from a variety of substances, such as corn, wheat, arrow-root, and potatoes. In one of the common processes employed, the starch is washed out of the moistened and finely divided substance by means of water, after which it is allowed to ferment in order to destroy some of the impurities present. Finally, it is washed in pure water by decantation.

The grains of starch exhibit under the microscope peculiar markings and forms which differ according to the source from which the starch was obtained. Thus the microscope is able to reveal the origin of any sample of starch as well as to expose any adulteration. The markings are more clearly brought out by treating the starch with dilute potassium hydroxide solution.

The largest grains of starch occur in the potato, while the smallest are found in rice.

When starch is heated to 205°, it is converted into an isomer termed *Dextrine*. This is much used as a substitute for gum arabic. The backs of postage stamps and the flaps of envelopes are gummed with dextrine.

When the starch is moistened with a mixture of dilute hydrochloric and nitric acids, the conversion into dextrine takes place at from 100° to 125°. In fact, most of the dextrine of commerce is prepared in this way.

247. The Gums, $(C_6H_{10}O_5)_n$. — Of the gums, gum arabic and gum tragacanth are well-known examples. Gum arabic exudes from several species of acacias, which are natives of tropical regions. These gums are used for making mucilage, confectionery, and inks, and for many pharmaceutical purposes.

Nearly every kind of wood and vegetable tissue carries gummy substances, which are usually soluble in water.

248. Cellulose, $(C_6H_{10}O_5)_n$. — Cellulose occurs in all plants, since it forms the basis of all cell-walls. But it seldom occurs pure, as some of the solids which the sap carries in solution are deposited in the cell-walls during the growth of the tissues.

Cellulose is of great importance, since it forms the bulk of many fibres which are used in enormous quantities. Among these fibres may be mentioned cotton, hemp, flax, and wood fibres which are extensively used for making cloth, cordage, paper, etc.

Gun-Cotton, or cellulose hexnitrate, $C_{12}H_{14}(NO_3)_6O_{10}$, is a powerful explosive prepared by first treating cotton wool with alkalies to remove gummy matters, after which it is

treated with a mixture of strong nitric and sulphuric acids. Finally, it is washed with much pure water until every trace of free acid is removed in order to prevent spontaneous decomposition, which is often accompanied by disastrous explosions. ·

Collodion is a solution of some of the lower nitrates of cellulose in a mixture of alcohol and ether. It is used in surgery and in photography.

249. The Glucosides. — Under this name are included a number of substances occurring in plants. On decomposition they yield a glucose together with other substances.

Amygdalin, $C_{20}H_{27}NO_{11} + 3H_2O$, occurs in bitter almonds, apple seeds, peach pits, etc.

Salicin, $C_{13}H_{18}O_7$, is found in the bark of willows, and in the bark and leaves of poplars.

The *Tannins* occur in the barks of certain trees, but more especially in the gall-nuts found on oak-trees. The tannins have the property of forming inks with ferric salts. They are largely used for that purpose, and for tanning leather.

CHAPTER XIX.

THE TERPENES, BENZENES, STYRENES, NAPHTHALENES, AND ANTHRACENES, AND THEIR DERIVATIVES.

THE TERPENES, C_nH_{2n-4}.

250. The Terpenes, $C_{10}H_{16}$. — Of this series of hydrocarbons, the turpentines, the camphors, and certain essential oils are among the best-known compounds.

Turpentine, $C_{10}H_{16}$, is the product of southern pine-trees, *Pinus australis*. Turpentine is also obtained in some parts of Europe. A tree is wounded, and the pitch which oozes out is allowed to collect in a box or pocket which is cut into the tree. In France a vessel is used to collect the pitch. From time to time the pitch is gathered up until a sufficient quantity has been collected, when it is subjected to distillation. The turpentine distils over, and the solid residue is sold under the name *Rosin*.

Ex. State the uses of turpentine.

When turpentine is acted upon by hydrochloric acid, a peculiar substance called *Artificial Camphor*, $C_{10}H_{16}HCl$, is produced. This substance closely resembles camphor.

Camphor, or *Laurinol*, $C_{10}H_{16}O$, is obtained by distilling with water chips of *Laurus camphora*, a tree growing in China and Japan.

Borneo Camphor, $C_{10}H_{16}O$, occurs in *Dryobalanops camphora*, a tree native to Borneo and the adjacent islands.

Belonging to the terpene series are a large number of essential oils that occur in various parts of different plants. Among these oils those of lemon, bergamot, neroli, mace, sassafras, bay, anise, fennel, peppermint, spearmint, lavender, and rosemary may be mentioned as consisting principally of terpenes.

Closely allied to the terpenes is *Caoutchouc*, or *Indian Rubber*, which consists of the dried milky juice of the *Jatropha elastica* and other kindred plants.

Vulcanized rubber contains from twelve to fifteen per cent of sulphur, and is prepared by heating caoutchouc with sulphur to about 150°. At higher temperatures *Vulcanite* or *Ebonite* is obtained.

Gutta Percha is the dried juice of a tree, *Isonandra percha*, a native of the East Indies.

THE BENZENES, C_nH_{2n-6}.

251. Benzene, C_6H_6. — This series is often called the *Aromatic Series*, since several fragrant compounds belong to it. The lowest known term is Benzene (not the commercial benzine, which is a mixture of paraffin hydrocarbons), or, as it is sometimes called, *Benzol*.

Coal tar has been mentioned as one of the by-products in the manufacture of illuminating gas; and it is from this source that benzene is chiefly obtained. The crude tar is subjected to fractional distillation. The "first runnings," which include all products boiling under 110°, contain small quantities of benzene. The "light oil," however, coming over between 110° and 210° contains benzene in larger quantities. From this light oil benzene is separated and purified by further fractional distillation and by treatment with sulphuric acid and caustic soda.

Benzene is a colorless, strongly refracting liquid, possessing a characteristic odor, and burning with a luminous but smoky flame. It boils at 80.5°. It serves as an excellent solvent for various fats, resins, alkaloids, etc., and it is extensively used in the manufacture of the aniline dyes.

Benzene forms both substitution and addition products; but in all these compounds all six carbon atoms appear. Various facts noted in the chemical behavior of benzene have led to the adoption of a graphical formula in which the carbon atoms are arranged in the form of a ring or closed chain, the carbons being connected alternately with one and two linkages. This formula may be represented as follows : —

$$
\begin{array}{c}
\text{H} \\
| \\
\text{C} \\
\diagup \quad \diagdown\!\!= \\
\text{H–C} \qquad \text{C–H} \\
\| \qquad\quad | \\
\text{H–C} \qquad \text{C–H} \\
\diagdown \quad \diagup\!\!= \\
\text{C} \\
| \\
\text{H}
\end{array}
$$
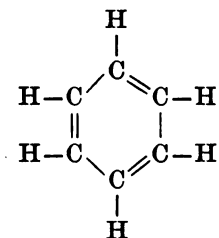
Now the substitution products of benzene are made by replacing one or more of the hydrogens, leaving the carbons undisturbed.

In the best known of the addition products, benzene acts like a hexad radical, thus: benzene hexchloride, $C_6H_6Cl_6$; benzene hexbromide, $C_6H_6Br_6$. To account for these compounds, the supposition has been made that one of each of the double links has been broken, thus giving up six bonds to new uses.

Since any one or all of the hydrogens of benzene may be replaced by a radical; and further, since the hydrogens of these substituted radicals may be replaced by elements

or radicals; and again, since each compound may have several isomers, it is evident that the derivatives to be obtained from benzene are simply innumerable.

Of the homologous series of which benzene is the first member, four members are known : —

Benzene	C_6H_6.
Toluene	C_7H_8.
Xylene	C_8H_{10}.
Cymene	C_9H_{12}.

We can here notice only a few of the most important compounds derived from this series.

252. Phenol, Phenyl Alcohol, or Carbolic Acid, C_6H_5OH. — Phenol, although a true alcohol corresponding to the hydrocarbon benzene, is quite generally known as carbolic acid. It is prepared from that fractional distillation product of coal tar which boils between 150° and 200°. The "middle oil" obtained between these temperatures is treated with caustic soda and afterward with sulphuric acid.

Now since phenol forms a hydrate with water which splits up into the pure acid and water upon distillation, this reaction is used for the final purification of the better grades of carbolic acid.

Phenol possesses a characteristic odor, is soluble in water, and when taken internally it is a violent poison. It is much used as a disinfectant.

Phenol forms a well-defined series of derivatives, among which is trinitrophenol, or *Picric Acid*, $C_6H_2(NO_2)_3OH$. Picric acid is a very bitter poisonous substance which is used alone for dyeing silk and woollen goods yellow. With other dyes it is used for producing different shades.

Picric acid is now manufactured by the action of nitric acid on phenolsulphonic acid, $C_6H_4(OH)SO_3H$, although it is to be had by the use of phenol and nitric acid.

253. Resorcin and Pyrogallol. — It will be noticed that phenol is a monad alcohol, but just as one would expect there are other benzene alcohols. *Resorcin*, $C_6H_4(OH)_2$, is a diad alcohol obtained by melting various resins with caustic potash. It is largely used in manufacturing dyes.

Pyrogallol, or *Pyrogallic Acid*, $C_6H_3(OH)_3$, is a triad alcohol obtained by subliming gallic acid at from 210° to 220°. It is found in commerce as lustrous, flaky, or acicular crystals. It is used as a reagent in gas analysis on account of the ease and rapidity with which it absorbs oxygen. It is also used in photography as a developer.

254. Nitrobenzene, $C_6H_5NO_2$. — Nitrobenzene is a light yellow, strongly refracting liquid which has an odor resembling the oil of bitter almonds somewhat modified by another odor suggesting oil of cinnamon.

It is manufactured in large quantities under the name of artificial oil of bitter almonds or essence of mirbane. It is prepared by treating benzene with a mixture of strong nitric and sulphuric acids. The 'crude oil is purified by passing through it a current of steam, after which it is treated with caustic soda and distilled with steam under pressure.

Although nitrobenzene is somewhat poisonous, and has an irritating effect on the skin, nevertheless it is used in perfuming the cheaper grades of soap. But the largest quantities are employed in the manufacture of aniline, aniline blue, aniline black, and magenta.

255. Aniline, Amidobenzene, or Phenylamine, $C_6H_5NH_2$. — Aniline is now manufactured in enormous quantities for use in preparing the aniline dyes. It is obtained by the action of nascent hydrogen on nitrobenzene. The nitrobenzene is placed in a large iron cylinder fitted with a stirring apparatus, and the hydrogen is furnished by adding directly to it hydrochloric acid and iron. The crude product is purified by distillation.

Aniline is a colorless liquid of a characteristic odor and possessing strong basic properties. It forms definite salts with the ordinary acids, and together with its compounds it is invaluable to the color industry. It acts upon the system as a powerful poison.

256. The Toluenes. — Toluene, C_7H_8, is obtained by distilling toluic acid with an excess of lime. It occurs naturally in petroleum, and can be obtained by various reactions upon benzene.

The *Cresols*, C_7H_8O, of which there are three isomers, occur in coal tar, pine tar, and creosote.

The toluene alcohol, C_7H_7OH, is called *Benzyl Alcohol*. It occurs in balsam of Peru and in balsam of Tolu.

The aldehyde of benzyl alcohol, C_7H_8O, or benzoic aldehyde, is the true *Oil of Bitter Almonds*. It occurs in a glucoside, amygdalin, one of the constituents of bitter almonds, cherry pits, laurel leaves, etc. Under the influence of emulsin, a ferment found in amygdalin itself, amygdalin breaks up into glucose, prussic acid, and oil of bitter almonds: —

$$C_{20}H_{27}NO_{11} + 2\,H_2O = 2\,C_6H_{12}O_6 + HCN + C_7H_6O.$$

Benzoic aldehyde on oxidation passes into *Benzoic Acid*, $C_7H_6O_2$, a monobasic acid occurring in gum benzoin and

the balsams of Peru and Tolu. It also occurs in the urine of herbivorous animals. Benzoic acid may be obtained in a variety of ways, but the best commercial article is obtained by subliming gum benzoin. Cheaper forms are prepared from the urine of cows and horses, and by the oxidation of toluene.

EXP. 103. Place a small quantity of benzoic acid in a beaker with no lip, and then fit a paper funnel over the mouth of the beaker. Place the apparatus on the sand-bath and heat gently. Note the sublimate of benzoic acid which collects inside the funnel.

Salicylic Acid, $C_7H_6O_3$, occurs as methyl salicylate in oil of wintergreen, from which it is prepared for commercial purposes. It is also prepared by treating benzene with caustic soda and carbon dioxide. Salicylic acid is now largely used as an anti-ferment and in medicine.

Gallic Acid, $C_7H_6O_5$, occurs in many plants, such as sumach, Chinese tea, and in nut-galls. It is prepared from nut-galls by the fermentation of the tannin which they contain.

Tannic Acid, $C_{14}H_{10}O$, also occurs in nut-galls, from which it is obtained for commerce.

Nitrotoluene, $C_7H_7NO_2$, is prepared by treating toluene with nitric acid. By reduction with hydrogen this substance is reduced to *Amidotoluene*, $C_7H_7NH_2$, which is a necessary constituent of the red and violet aniline colors. This substance occurs as an ingredient of commercial aniline.

There are three isomeric *Xylenes*, C_8H_{10}, all to be obtained from coal tar. *Cymene*, C_9H_{12}, occurs in oil of caraway and in oil of thyme. It can be prepared from the terpenes.

Closely related to the benzene derivatives is the common substance known as *Indigo*. The indigo plants are natives of tropical countries. From them indigo is prepared by placing the plants in tanks and covering them with water. Fermentation sets in, and when it is completed the water solution is drawn off, carrying the coloring-matter in solution. Upon standing, the indigo is precipitated, when it is collected, pressed, and dried ready for the market. The value of indigo depends upon the amount of *Indigo Blue*, or *Indigotin*, $C_{16}H_{10}N_2O_2$, which the crude article contains. Indigo is now prepared artificially.

THE STYRENES, OR CINNAMINES, C_nH_{2n-8}.

257. Styrene, or Cinnamine, C_8H_8. — This hydrocarbon occurs in liquid storax, a fragrant, honey-like substance which yields styrene upon distillation with water and sodium carbonate.

Styryl alcohol, $C_9H_{10}O$, belongs to this series, and its aldehyde, cinnamic aldehyde, $C_9H_8O_2$, constitutes the greater part of the essential oil of cinnamon. Cinnamic acid, $C_9H_8O_2$, closely resembles benzoic acid. It occurs in storax and in balsam of Peru. This acid is now manufactured on the large scale by treating benzyl chloride, $C_7H_6Cl_2$, with sodium acetate.

THE NAPHTHALENES, C_nH_{2n-12}.

258. Naphthalene, $C_{10}H_8$. — This hydrocarbon occurs in large quantities in the heavier portions of coal tars, boiling between 180° and 220°. It crystallizes in large pearly plates. From careful studies of the chemical behavior of naphthalene it has been discovered that this hydrocarbon consists of two benzene residues which con-

tain two carbons in common. The following formula will show its constitution : —
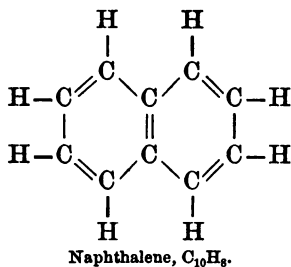
Naphthalene, $C_{10}H_8$.

Naphthalene forms many derivatives, and among them are some of the most beautiful dyes. Thus Martius' Yellow, $C_{10}H_5OH(NO_2)_2$, Naphthol Yellow S., $K_2C_{10}H_4N_2SO_8$, and other splendid colors belong to this series.

THE ANTHRACENES, C_nH_{2n-18}.

259. Anthracene, $C_{14}H_{10}$. — Anthracene is prepared from those portions of coal tar boiling between 340° and 360°. It crystallizes in white, silky scales or plates, and like naphthalene it furnishes beautiful dyes. Its constitution is exemplified by the following formula : —
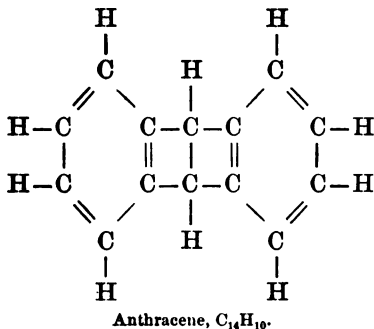
Anthracene, $C_{14}H_{10}$.

Among the dyes derived from anthracene we may mention Alizarin, $C_{14}H_8O_4$, and Purpurin, $C_{14}H_8O_5$. These substances are found naturally in madder root, which has been used from the earliest times as the source of a red dye. Formerly large tracts of land were devoted to the cultivation of the madder plant, but now Turkey Red, as this dye is called, is nearly all obtained from coal tar.

THE ALKALOIDS AND THE ALBUMINOIDS.

260. The term **Alkaloids** is applied to a class of substances contained in a large variety of plants, and especially those containing medicinal and poisonous principles. Our knowledge of the constitution and relations of these substances is extremely limited, and in most cases entirely wanting.

The alkaloids are optically active on polarized light; some being dextro-rotary, and some being lævo-rotary. In their chemical behavior they resemble the amines and the amides; and they all contain carbon, hydrogen, and nitrogen, and nearly all contain oxygen.

They are nearly all crystallizable, especially those that are solids ; and they form crystallizable salts with the ordinary acids.

Conine, $C_8H_{15}N$, the active principle of poison hemlock, and *Nicotine*, $C_{10}H_{14}N_2$, the active poison found in tobacco, are liquids. These are among the most important of the liquid alkaloids.

Caffeine, $C_8H_{10}N_4O_2$, is found in tea and coffee, and in other plants that are used to prepare infused beverages. *Theobromine*, $C_7H_8N_4O_2$, is found in cocoa.

Opium, the dried sap of certain species of poppies, furnishes about nineteen different alkaloids, which possess more or less active properties. Among the more noteworthy are *Morphine*, $C_{17}H_{19}NO_3 . H_2O$; *Codeine*, $C_{18}H_{21}NO_3$;

Thebaïne, $C_{19}H_{21}NO_3$; and *Narcotine*, $C_{22}H_{23}NO_7$.   The sulphates of these alkaloids are most used.

Cinchona bark furnishes about twenty-one alkaloids, of which *Quinine*, $C_{20}H_{24}N_2O_2$, and *Cinchonine*, $C_{20}H_{24}N_2O$, are the most important.   The sulphates and chlorides of these alkaloids find extended use.

Nux vomica furnishes the powerful poisons, *Strychnine*, $C_{21}H_{22}N_2O_2$, and *Brucine*, $C_{23}H_{26}N_2O_4 . 4 H_2O$.

The reader is referred to any of the standard works on pharmacy, or to the dispensatories, for lists and descriptions of the crude drugs and alkaloids used in medicine.

261. The **Albuminoids** are compounds of very complex constitution, concerning which our knowledge is quite incomplete.   They do not crystallize, but exist in an amorphous, jelly-like form; and in consequence it is nearly impossible to obtain them in a state of sufficient purity to enable us to determine with exactitude the proportions in which their constituents unite, or even to be certain what elements are present in the pure compounds.

Nevertheless, these compounds are of great importance to both plants and animals.   In plants they occur in nearly every part, but more especially in the seeds.   In young and growing plants, particularly those used as food for man and animals, the albuminoids are quite generally distributed throughout the tissues.

Gluten is the albuminoid found in grains, and is a sticky, elastic substance which gives tenacity to dough.

Albumen is found, in the purest form, in the whites of eggs.   This substance may be obtained, as a flocculent precipitate, by adding acetic acid to the white of an egg, and then diluting with water.   Albumen also occurs in the serum of blood.

Fibrin may be obtained from fresh blood by whipping it with a bundle of twigs. Fibrin, when thus obtained, and after washing with water, appears in the form of whitish threads, which are tasteless and insoluble in water. Fibrin remains in solution while the blood is circulating through its proper channels; but on removing the blood from the circulation, the fibrin immediately causes coagulation.

Casein is the albuminoid found in milk, and separates out as curd when the milk becomes sour.

The albuminoids possess in common the property of coagulating, upon the application of heat, or by contact with alcohol. They readily undergo putrefaction, and in other respects their resemblances are close.

They all contain sulphur, and many of them contain phosphorus, beside carbon, nitrogen, hydrogen, and oxygen. No formula can, with certainty, be assigned to albumen.

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